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**Cover 1: *Taxodium distichum* with *Tillandsia usneoides* (moss).
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STEM CELLS TEST - RECOMMENDATION OF ECVAM FOR CHEMICAL TESTING WITH CONSEQUENCE IN HEALTH RISK ASSESSMENT

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ABSTRACT. The introduction of stem cells in environmental health studies could mean an important step in health risk assessment. It may be all the more important as we attend to increase the environmental influences to disease -associated epigenetic changes among adults, but especially for children. The assessment of health risk requires testing of environmental chemicals which they continued to need more time in animal studies. The stem cells -human models, increase the rate of testing, that does not require dose translation across species. Validation of environmental exposure will be done for very large interval data, for many chemicals or "chemicals cocktails" at much lower costs.

Key words: *stem cells, alternative methods, chemical testing.*

STEM CELLS DIFFERENTIATION - WHERE, WHEN, HOW?

The epigenetic changes are the molecular basis for long-term effects of the environment on disease development (Ospelt and Gay, 2014). For example, methylation or demethylation related the cells exposure; modulate the expression of CXCL12 with consequence on CpG nucleotides methylation - significantly correlated in the mRNA expression (Karouzakis et al., 2011).

The study of environmental health on "single cells" -like stem cells, gives us the chance to understand more precisely how environmental factors interact with genetic ones.

Stem cells are cells with high capacity of multiplication in particular conditions. These cells are capable to differentiate in a wide variety of other cells, which is why they are also called pluripotent cells. The first stem cells have been observed in the mouse embryonic extract in 1980, but the effective its isolation was performed latest in 1998. Then, for the first time was observed their ability to transform themselves into a variety of specialized cells. The epigenetic landscape during the cells development is the emergence of different cells lineage (Aiba et al., 2009).

Thus can be obtained the liver cells, the kidney cells, cardiomyocytes, neural cells, etc., which are generally difficult to grow in the laboratory using conventional techniques. Stem cells can divide symmetrically and produce other stem cells or can divide asymmetrically producing the cells with very well determined fate. The switch between the two paths and the involved mechanisms are still not well understood, figure 1.

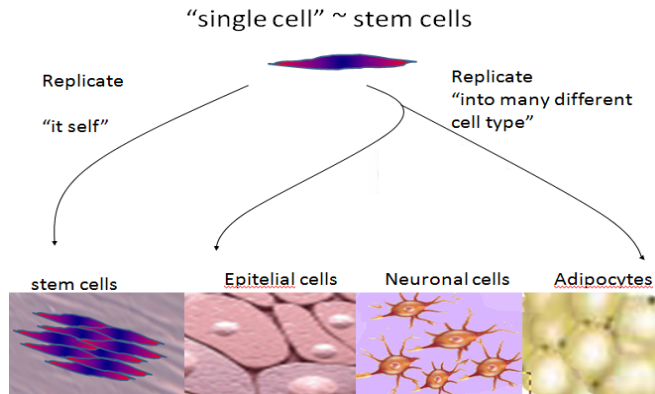


Fig.1. *Symmetric and asymmetric multiplication of stem cells*

In present, we are at the moment of awareness the relevant interaction genes-environment, in other words epigenetics effects on human stem cells model trying to understand how these cells can be involved to define the sensitivities, the susceptibility age dependent or differential population (Casado et al., 2011; Gasiewicz et al., 2017).

STEM CELLS TEST - RECOMMENDATION OF ECVAM FOR CHEMICAL TESTING WITH
CONSEQUENCE IN HEALTH RISK ASSESSMENT

Testing of toxicity using stem cells is already in use for different types of exposures.

In chemical exposure, highest interest was in changing the cells contractility due to direct effect of the substance on stem cells. Looking at the cardiomyocytes obtained after the rabbit stem cells differentiation Yazawa et al. (2011), observed that chemical compounds inducing arrhythmia and with effect on electric signal transmission through Purkinje network has similar effect on differentiated cells, when contractility was tested through similar method with those measuring the heart function.

The answer of differentiated stem cells to a wide range of neurotoxic compounds has been studied on neurons, (Betts, 2010) and glial cells to which increase the incidence of autism (Dolmetsch and Geschwind, 2011).

The toxicity of chemical "cocktails" has been also followed on stem cells.

Tox 21, is the program by which the chemicals are tested to improve environmental health and pharmaceutical safety. The following direction could be of interest: cell line selection for high throughput transcriptomics (HTT); profiling environmental, drug, and food-related chemicals that inhibit acetylcholinesterase activity; predictive modeling of developmental toxicity with human pluripotent stem cells; toxicodynamic variability in developmental neurotoxicity; performance based validation of alternative test systems and models; retrofitting existing Tox21 high-throughput screening assays with metabolic capability; expansion of pathway coverage by Tox21 high-throughput screening assays for better prediction of adverse drug effects; development of high-throughput assays to detect chemicals with the potential to induce skin sensitization, eye irritation, or corrosion (EPA, 2017; Thomas et al., 2018).

According with the Interagency Coordinating Committee on the Validation of Alternative Methods, the validation of stem cells used as model will be in comparison with the most relevant current methods, based on the knowledge of human physiology.

Stem cells damage is followed in many other studies based on the inducing of oxidative stress in correlation with xenobiotics metabolism network. The magnitude of apoptosis, cells differentiation in relation with xenobiotics removing has been done (Cieślak-Pobuda et al., 2017).

The advantages of toxicity studies in correlation with cell biology methods focused on end points and stages of life, are presented by Committee on Toxicity Testing and Assessment of Environmental Agents, NRC (2007).

A very important aspect in the future, in toxicology will be to use human cell line-stem cells and cells components, for chemical testing. Testing of chemical teratogenity has been already validated on mouse, embryonic stem cells and is included in screening programs (Ahr et al., 2008; Paquette et al., 2008).

ToxCast neurotoxicity program, EPA's Endocrine Disruption Screening Program (EDSP) has in study thousands of chemicals - with biological activity, and generates data and predictive models on thousands of chemicals using stem cells.

CONCLUSIONS

In conclusion, if the effect of environmental factors on human is analyzed today from perspective of the observed effects on human health, interesting for the future would be the examination of stem cells and respectively, its differentiation process like model for different kind of exposures. End points will be particularly to exposure mark; so it will be different for indoor ambient pollutants -lung exposure, compared with ingested xenobiotics - liver exposure, or stored organochlorinated compounds - fatty tissues exposure, etc. In all these situations must be, included the cell's answer due to exposure sensitivities and individual susceptibility for assessing the real human health risk.

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THE IMPACT AND THE RISK OF ABANDONED BUILDINGS FROM PETROȘANI CITY ON THE URBAN ENVIRONMENT

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ABSTRACT. The city of Petroșani, as well as the whole area known as Jiu's Valley, is integrated in a general vision of transforming a mining region into a tourist destination and, in this context, the aspects related to the quality of the urban landscape must be taken into account in a very serious manner. Although most people, when they hear about landscape, think of the wonderful areas surrounding Petroșani city, the urban landscape should not be ignored either, this being the first that comes in contact with the tourists who will visit this region and will contribute to the economic well-being of the inhabitants. The present paper analyzes the impact of abandoned buildings on the urban landscape (environment) having as a starting point a reality valid in many former industrialized regions, namely that due to the countless restructuring, the population is constantly decreasing and one of the common consequences is represented by the large number of abandoned buildings, in different stages of degradation. These buildings, besides the fact that they strongly degrade the urban landscape (environment), often represent true outbreaks of infection and a real public danger, being exposed to the risk of arson or collapse. For this purpose, we have adapted the methods for identifying/ estimating the anthropic impact on the environment (the network method and the impact/risk matrices) for the situation under study.

Key words: *Petroșani, urban environment, abandoned buildings, impact.*

INTRODUCTION

In order to understand the reason why in the urban environment of Petrosani city more and more abandoned buildings have appeared, we must briefly present the demographic evolution and identify the reasons underlying this evolution.

According to the census from 2011, the population of Petrosani city rises to 37,160 inhabitants, decreasing from the previous censuses of 2002, when there were 45,195 inhabitants and from 1992 when the number was of 52,390 inhabitants, and the tendency of the last 8 years is the same, in decrease (***, 2014).

Correlating these data with the socio-economic evolution of the city, we cannot fail to observe that the main change is represented by the restructuring of the Romanian industry as a whole, and, especially the extractive one. In fact, we can say that everything starts from here, the restructuring of the mining sector (in particular coal exploitation) and the related ones (mining machinery and equipment companies, institutes and design-research-development companies in the field, etc.) started in the mid-90s. This restructuring also meant a first wave of migration but also a worsening of the socio-economic situation of the population in the area.

Restructuring of the mining sector has not only led to a decrease of the employees in the field and in those directly related, but also to a restriction of the activities in other sectors (services and utilities, public food, education, health, etc.), practically being seriously affected the zonal economy and encouraged labor migration. Of course, this process continues today and in conjunction with the lack of jobs in alternative sectors leads to a continuation of the phenomenon of labor migration to other cities and regions of the country with a much higher economic potential (Faur et al., 2017).

However, we should not neglect the fact that migration is also a worrying phenomenon for Romania as a whole, with many choosing to leave the country for destinations in Western Europe in search of a better life (Ianoş, 2004).

In the context of those presented, it is easy to understand why abandoned buildings have appeared and continue to appear in the urban landscape of Petrosani city.

MATERIAL AND METHODS

Location of the investigated area

The city of Petrosani is located in the central part of Romania, in the south of Hunedoara county (figure 1), at the confluence of the East Jiu with the West Jiu, geographically at the latitude of 45°24'44" north and the longitude of 23°22'24" east (***, 2014).

Outside the town of the same name, the municipality of Petroșani has the following localities in administration: Peștera Bolii, Dâlja Mare, Dâlja Mică and Slătinoara.

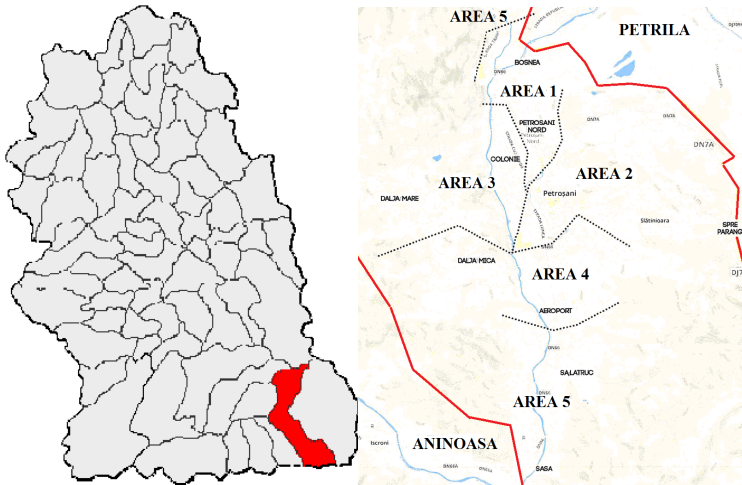


Fig. 1. Location of Petroșani city within Hunedoara county and its areal divisions (***, 2014)

It is the most important city within the Jiu Valley Basin (Petrosani Depression). It has an administrative area of 19,556 ha (195.56 km²), being located between the Retezat and Sebeș mountains (component unit of the Șureanu Mountains) to the north, the Vâlcan Mountains to the south, Godeanu to the west and Parâng to the east (Faur, 2018).

The relief of Petroșani city is typical for mountain depressions (figure 2), it is located at an altitude of 615 - 620 m, the highest altitude in the area being recorded in the Parângul Mare Peak (2519 m) and the smallest at Livezeni (the riverbed of East Jiu is at an altitude of 560 m) (Faur, 2018).



Fig. 2. *Panoramic view of Petroșani city (photo by: Daniela Baciu)*

Petroșani city is located on two important communication routes: DN 66 (E 79) Târgu Jiu - Simeria at the intersection with DN 66A Petroșani - Uricani - Câmpu lui Neag, with extension to Herculanu and DN 7A connecting the city to Valea Oltului, Petroșani - Voineasa - Brezoi) (Negoe, 2019).

Regarding the distance to the big cities, the city of Petroșani is located at 370 km from the country's capital, Bucharest, and 91 km from the capital of Hunedoara County, Deva city. Other important cities near it are: Târgu Jiu - 56 km, Craiova - 161 km, Timișoara - 250 km, Alba Iulia - 200 km, Sibiu - 220 km (***, 2014).

Short history

The official story of Petroșani begins in 1788, when the name is recorded in the book "Journey from Postdam to Constantinople" by Prussian officer Gotze. Only in 1818 the name of Petroșani town is mentioned in official documents, with the census attesting the presence of 233 inhabitants, whose main occupation was sheep breeding (***, 2014).

After 1840, the region will experience a rapid development, as the surface exploitation of coal discovered in the area begins. The mining basin would become the largest coal field in Romania and one of the most important in Europe (***, 2014).

Starting with 1848, the development of the locality is closely linked to the development of the mining industry. In 1918, after the Great Union, the

Petroșeni region is included in the new territorial-administrative organization of Hunedoara County. Until 1920, Petroșani was known as Petroșeni (a name still kept today by the natives peasant, the so-called "momârlani"), but from February 14, 1921 the settlement will become as we know it today, namely Petroșani.

On January 4, 1924, Petroșani commune becomes a town, and on March 1, 1968 it becomes a city (municipality).

Also, since 1948, the city of Petrosani becomes a university center, by establishing the "Coal Institute", today the University of Petrosani, which was to become one of the most prestigious higher education institutions with mining profile in Romania and Europe.

On the other hand, at present, on the administrative territory of the city is the Livezeni Mining Exploitation (located on Lunca street, no. 153), the headquarters of the Hunedoara Energy Complex (Timisoara street, no. 2), but also a museum, the only one in the country with a mining technique profile, the Mining Museum (Nicolae Bălcescu street, no. 2), and since 1949, Petrosani has hosted one of the most prestigious research institutions in Romania, "Testing Station for Mining Security - a subsidiary of ICEMIN Bucharest ", currently the National Institute for Research and Development for Mining Security and Explosive Protection (INSEMEX) (General Vasile Milea street, no. 32-34) (***, 2014).

The urban patrimony

The development of tourism activities in Petrosani, as an alternative to mining, involves, beyond the completion of the project "Development of the Parâng ski area" and its promotion, the arrangement and maintenance of the urban area (urban landscape/environment), so that it fits into the general vision.

According to official data, in Petroșani city there are almost 30,000 taxable buildings, the public and private patrimony, owned by the community of Petroșani being composed of the following assets (Negoe, 2019):

a) public: 19 roads; 150 streets; 34 bridges; 11 parks (respectively: Carol Schreter Central Park; European Community Park; Ion Luca Caragiale Park; Anghel Saligny Park; Romtelecom Park; Pensioners Park; Avram

Iancu Park; Spring Park; Pistruiatul Park; Micropiața Park; Peace Park); 11 green areas; 116 car parks; 29 children's playgrounds; 1 stadium - Jiul Stadium; 2 cemeteries; 7 buildings and lands where the Local Council and the City Hall operate; 118 social housing; 467 dwellings housing; 16 ANL dwellings; 4 traffic lights; 6 roundabouts.

b) private: forests, with a total area of 11,721 ha; pastures, with a total area of 3,082 ha; means of transport 17; fixed assets and inventory items in the accounting records.

According to the list of the Ministry of Culture, the following historical monuments exist on the administrative territory of Petrosani city (***, 2014):

➤ The first headquarters of the Romanian Petroșani Joint-stock Company, founded in 1920. At present, the building houses the Petroșani Mining Museum. Address: Str. Nicolae Bălcescu, no. 2;

➤ The headquarters of the Mining Trade Union between 1921-1946, at present is the social canteen. Address: Str. Cuza Voda, no. 6;

➤ The wooden church of the Holy Archangels (Sânonilor), built in the 18th century. Address: Str. Lunca, no. 8;

➤ The Officials Casino, built in 1905, houses the Dramatic Theater I.D. Sîrbu. Address: Str. Mihai Viteazul, no. 2;

➤ Prince Mircea dispensary, established in 1925, is today the headquarters of the Petroșani Students Cultural House. Address: Bd. December 1, 1918, no. 62;

➤ The Workers Casino, inaugurated in 1925. Currently the La Belle Epoque Restaurant. Address: Str. Grivița Roșie, no. 38;

➤ The "Colonia Workers Housing" neighborhood was created at the end of the 19th century, today it is known as the Colony Neighborhood. The Colony Housing District was included in the list of D.M.A.S.I. in the category "urban historical area". Location: the neighborhood is bounded by the East Jiul river, Cărbunelui (Coal) street, railway station and CFR lines, Vlad Țepeș street.

➤ The historical center of the city (between Victoriei Square and the Civic Center), dating from the end of the 19th century. Location: Mihai Viteazul (Michael the Brave) street.

It should be noted that these buildings cannot be considered as monuments in the true sense of the word, the spectacular architectural elements being poorly represented (Dura and Nistor, 2014).

Description of the studied abandoned buildings

It is practically impossible to include in this study all the abandoned buildings in Petrosani city and for this reason we have selected a number of 6 buildings, which we considered to be representative and which can best highlight the impact and risk manifested on the urban environment.

B1. Former Military Unit 01032 (private property, area 1) - constructed in the central area, is ruined on the day that passes, without the authorities being able to intervene (figure 3).



Fig. 3. *Former Military Unit 01032*

Restituted, the building in question housed the Military Unit 01032, and is located on Timișoara street, at number 5, in the city of Petrosani. In the building that has an area of 335.44 m², as well as an interior courtyard of 279.27 m², the City Hall intended to move the Community Public Service for the Evidence of Persons.

In the end, the one storey building, with 18 rooms and two bathrooms, being requested and received by the descendants of the former owner has no other destination. In the meantime, the "central pavilion" building was immediately struck by the thieves of building materials. Over the years, from here almost everything that could be stolen was stolen. The terracotta stoves in the 18 rooms were broken, completely disappearing. On the same street, in the center of the city, there are other buildings, all being restituted to former owners or their descendants, that are now trampled by thieves.

It should be noted that in addition to the danger it poses for passers-by, periodically pieces of plaster, bricks and tiles falling from the building, there is also the danger of arson and its propagation in the neighboring buildings. In fact, in the last 5 years, firefighters were forced to intervene 4 times in order to extinguish fires caused by those who sheltered in these ruins and tried to warm themselves.

Also, because of the homeless, more precisely the dejections and household waste generated by them, the area has also become an outbreak of infection.

B2. Petroșani Central Workshops/IUMP/UMIROM/GEROM (private property, area 3) - at the north entrance in the city of Petroșani, between Dărănești and Petroșani Rail Station, we are greeted by the ruins of what was once an important mining equipment company in Romania.

Beyond the importance on the industrial and socio-economic level (here being employed more than 3,500 people at one time), some of the buildings now abandoned are loaded with history, here being cast the famous Infinity Column, a masterpiece of the famous sculptor Constantine Brancuși.

Today, with the exception of the building located at gate 1, which functions as an event hall, from the former company a few workshops still operate (whose days are counted), the rest being practically abandoned (figure 4). And in this case we are also talking about a private property about which we weren't able to obtain much information.



Fig. 4. *Petroșani Central Workshops*

Of course, the "restructuring process" of mining in the Jiu Valley is one of the main causes of the decline of this symbol of Petroșani, but we cannot fail to notice the complicity and lack of interest of those who have taken over the company's assets through privatization.

This industrial objective could easily be rethought and integrated into the local and national economy. Even if there is no demand for mining machinery, equipment and subassemblies, a wide range of products for other industries and for general use could be produced here.

Some of the old buildings could easily have been passed in the Industrial Heritage of Romania together with some of the equipments (on the model of the former buildings of Petrila mine) and could have gained a later destination (even introduced in a wider industrial tourist circuit, developed throughout the entire Jiu Valley).

B3, B4. CONSMIN buildings (private property, area 3) - as the company name suggests, it had as object of activity mining constructions and, as expected with the restructuring of the activities in this sector, the company went bankrupt.



Fig. 5. CONSMIN buildings on Mihai Eminescu street (a) and Cărbunelui street (b)

Two of the buildings (located on Mihai Eminescu and Cărbunelui streets) were abandoned, at present being in a state of ruin and constituting a real public danger for passers-by (by collapsing of constructive elements) (figures 5.a and 5.b).

B5. CFR (Romanian Rail Ways) Deposits (CFR patrimony, area 3) - located at the north exit from Petrosani Rail Station, on the left side on the direction towards Simeria, these deposits have not been used since the early 90s (figure 6).



Fig. 6. *CFR deposits*

For a long time in these buildings, the needy people in the Colony District found their shelter turning them into real outbreaks of infection and causing some small fires.

At present the structure of resistance is severely affected, the roof presenting an imminent danger of collapse, was abandoned by people, being "taken over" by homeless animals.

B6. Former Military Unit 01032/Former Gendarmerie (in the patrimony of the Ministry of Internal Affairs, area 3) - the building is also located in the Colony District, on Vlad Țepeș street and after the military unit 01032 was disbanded it was taken over for a long time by the Romanian Gendarmerie.

At the moment it is completely abandoned and like many other buildings it has been trampled by thieves of building materials.

However, being a newer building, with concrete structure, the resistance elements and the exterior walls are presented under acceptable conditions, which is why we consider that it could be used for another purposes (figure 7).

Moreover, another similar building, which belonged to the same military unit, was transferred to Petrosani City Hall and transformed into a building with social housing.



Fig. 7. Former Gendarmerie

In reality, in Petroșani city, there are a multitude of abandoned buildings (housing buildings especially in Airport neighborhood, residential houses, industrial buildings and structure, former thermal distribution points, etc.), which are in different stages of degradation and can be considered as factors of impact and risk on the urban environment.

In addition to these, there are also a number of buildings whose status is uncertain (such as the “New” Students Cultural House, whose construction began in 1992 and has not been completed), with the intention that they will assume different functions, but which at the moment contributes to the degradation of the urban environment of the city.

In the rest of the paper the references to the abandoned buildings taken in study will be made through the abbreviations B1 - B6.

RESULTS AND DISSCUTION

According to a previous study (Buia and Nimară, 2019), based on the recommendations in the specialized literature (Baciu, 2014; Bold and Nimară, 2016; L.I. and I.E.M.A., 2013; *** 2000;), the urban landscape of Petroșani municipality fits in the category of distinct landscapes, in which the localities have a predetermined plan or are developed organically, with a clear structure, the presence of craftsmanship skills, recognized outside the local community,

average number of pictures, paintings or postcards of the available landscapes, one or more recognized events for traditional features, relatively stable urban dynamics, with very few changes in recent years, a few industrial constructions in operation, a few new constructions, recent beginning of an urbanism system, few historical monuments, good accessibility (one or more national roads or railway transport of medium-good quality);

In this general context, for the identification and quantification of the impact we used a well-known instrument (impact matrix), adapted for the present study, and also for the evaluation of the risk that these buildings present for the urban environment, we used a simplified procedure, adapted according to the legal regulations in force (***, 1997).

Impact assessment by matrix method

The matrices are made up of double entry tables, in which, on lines, usually, the environmental components and factors involved, divided and grouped into categories are written, and in the columns are written the elementary actions in which the impact generating activity was broken down. Each intersection of the matrix represents a potential impact relationship between the causal factors and the components of the environment (Lazăr and Faur, 2011).

Generally, the most used are the quantitative type matrices, which aim to evaluate, through a numerical score, both the individual impacts and the overall impact of the project, and are constructed by assigning to each crossing point a numerical coefficient that expresses the importance of that interaction compared to the others. In this case, the matrices become operative tools of the impact analysis and evaluation phase (Lazăr and Dumitrescu, 2006; Lazăr and Faur, 2011).

In order to identify and quantify the impact of abandoned buildings in the city of Petrosani on the urban environment, we built a matrix (table 1) in which, on lines, we have the buildings identified and described in the previous paragraph (the 6 buildings), and on the columns we have the types of degradation and the dangers that they represent (7 categories: a - the state of the resistance structure; b - the external appearance; c - the internal appearance; d - the stability of the constructive elements; e - the danger of arson (the presence of combustible elements); f - the presence of the waste/outbreaks of infection; g - flooded spaces).

The last column presents the average impact that each of the analyzed buildings has on the urban environment. The value of the average impact is important for the last subchapter, the one assessing the risk that these buildings represent for the urban environment and implicitly for the most important component of it, humans.

Since we cannot talk about a positive impact of the abandoned buildings on the urban environment, the following values were adopted for the construction of the matrix (Negoe, 2019):

0 - no impact (not applicable for the analyzed building);

1 - minimum impact:

a - there are no indications that certain elements of the resistance structure may be affected, no detailed specialized investigations are necessary (a visual inspection by a specialist in structures is sufficient);

b - visible areas affected by infiltration, lack of small plaster fragments, inscriptions (graffiti), discolored areas;

c - visible areas affected by infiltration, lack of small plaster fragments, inscriptions (graffiti), discolored areas, local cracks in walls, ceilings, steps, etc.;

d - no drops of plaster blocks, bricks were reported, but isolated tile drops caused by snow sliding were reported;

e - wooden structures and flammable materials are reduced in volume and their distribution in the building does not allow the generalization of a fire;

f - there are waste materials in the building, but these are not organic in nature, dejections are not reported, rodents and insects have been reported;

g - water accumulates in some rooms during torrential rainfall, but it evaporates shortly.

2 - medium impact:

a - the elements of the resistance structures are seriously affected, there is a need for thorough specialized investigations, resistance tests;

b - large areas affected by infiltration, lack of large plaster fragments, inscriptions (graffiti), large cracks visible on the outside;

c - large areas affected by infiltration, lack of large plaster fragments, inscriptions (graffiti), pieces detached from walls, ceiling and steps, cracks extended into walls, ceilings, steps, etc.;

d - periodic drops of plaster blocks, bricks and tiles were reported;

e - wooden structures and flammable materials are extended in volume (25 - 50%), and their distribution in the building allows the generalization of a fire;

f - in the building there are important volumes of organic waste, human and animal dejections are reported, colonies of rodents and insects are present;

g - certain rooms (basement) are partially flooded, the water is infected, it has a strong unpleasant smell and does not evaporate throughout the year.

3 - major impact:

a - the resistance structure is irreparably affected, the collapse of the building is imminent and represents an active danger for pedestrians and vehicles in the area of influence;

b - appearance of ruin, absence of plastering on more than 50% of the outer surface, lack of portions or fragments from the outer walls, building covered by spontaneously installed vegetation;

c - obvious infiltration (practically it rains in the building), absence of plastering on more than 50% of the interior surface, inscriptions (graffiti), partially or totally collapsed walls, lack of pieces of roof, ceiling and floors, partially or totally collapsed steps, etc.;

d – daily falls of plaster blocks, bricks and tiles;

e - wooden structures and flammable materials are expanded in volume (> 50%), their distribution in the building allows the generalization of a fire, there have been fires in the past, they can extend to neighboring buildings;

f - the building is practically an improvised waste deposit, large quantities of human and animal dejections, colonies of rodents and insects are present;

g - the basement of the building is completely flooded, the water is infected, it has a strong unpleasant smell and it does not evaporate throughout the year.

Table 1. *Impact assessment/evaluation matrix*

Impact matrix	Impact factors (type of degradation – danger)							*AVERAGE IMPACT
	a	b	c	d	e	f	g	
B1	3	2	3	3	3	3	1	**3
B2	1	2	2	1	0	1	0	1,4
B3	3	3	2	3	2	2	0	**3
B4	3	3	3	3	0	1	0	**3
B5	2	3	3	3	3	3	1	2,57
B6	2	2	3	2	2	2	1	2

* The average value of the impact is calculated without taking into account the cells marked with 0. For example, in the case of an abandoned building that does not have a basement, there is no problem of water accumulation, but at the same time the building may have the resistance structure severely affected and a high risk of arson. Therefore, even if water is not a problem, it does not necessarily mean that the danger posed by that building is lower than in the case of a building in which the temporary or permanent presence of water is reported;

** If for the state of the resistance structure the awarded score is 3, ie major impact, then automatically and the average impact for the respective building will be considered equal to 3.

Depending on the scores obtained by the analyzed buildings in table 1 (the impact that these buildings have on the urban environment), we can establish 4 intervals according to the type of interventions required:

= 1 → buildings with minimal impact on the urban environment, requires cosmetic works/current maintenance (green);

> 1 - 2 → buildings with medium impact on the urban environment, requires renovation of the exterior and interior, inspection of the resistance structure, sanitation (B2, B6) (yellow);

> 2 - 3 < → buildings with major impact on the urban environment, requires immediate intervention to the resistance structure, extensive works of restoration of the exterior and the interior, sanitation, elimination of the arson risk (B5) (orange);

= 3 → public danger buildings, the impact is maximum, saving these buildings is not justified from the point of view of historical or architectural value and must be removed immediately (demolished) from the urban landscape/environment (B1, B3 and B4) (red).

Risk assessment

Certainly these buildings are at the same time a risk factor for the population of Petrosani city.

There is a wide range of different methodologies for risk assessment associated with objectives, both quantitative and qualitative. For the present study we have chosen the general methodology for risk assessment in accordance with Annex 4 of Order 184/1997 for approving the procedure for carrying out environmental surveys (***, 1997).

The risk is the probability of a negative effect occurring within a specified period of time and can be reproduced in the form of the equation:

$$\text{Risk} = \text{Danger} \times \text{Exposure}$$

Risk assessment involves an estimation (including hazard identification, magnitude of effects and manifestation likelihood) and risk calculation (including quantifying the importance of hazards and consequences for persons and/or affected environment). The overall objective of the assessment is to control the risks on a site by identifying:

- the most important dangers;
- resources and recipients at risk;
- the mechanisms by which the risk is realized;
- the important risks that appear on the site;
- the general measures needed to reduce the risk level to an acceptable level.

The qualitative assessment of the risk will take into account the following factors: danger/source; the drive path; target/receiver (which may include human beings, animals, plants, water resources and buildings).

The degree of risk depends both on the nature of the impact on the receiver and on the probability of manifesting this impact.

Risk calculation/quantification can be based on a simple classification system where the probability and severity of an event are ranked upwards, assigning them a random score (table 2).

Table 2. *Simplified system for classification of severity a probability*

Simplified model	
Severity (danger)	Probability (exposure)
1 = small (minimum)	1 = small (reduced)
2 = medium	2 = medium
3 = major	3 = high

The risk can then be calculated by multiplying the probability factor with the severity factor in order to obtain a comparative figure. This will allow comparisons between different risks. The higher the result, the higher the priority that must be given to risk control.

Starting from this, we have designed a risk assessment method, starting from the values obtained for the average impact, presented in table 1.

Thus, we considered that these values can be equivalent to the danger posed by these buildings, and the exposure is determined according to the area in which they are located (see figure 1 and the description of the studied buildings). Basically, the areal divisions of the territory of Petroșani city was made based on aspects such as: the presence of heritage, administrative, socio-cultural and educational buildings, accessibility and distance from them, the quality of the infrastructure, parks and recreation areas, pedestrian and auto traffic etc. (***, 2014; Negoe, 2019).

Based on these considerations, we set a scale from 1 to 3 for the exposure (1 small (reduced) exposure, 2 medium exposure and 3 high exposure) as follows:

- 1 - corresponding to area 5 of the city;
- 2 - corresponding to areas 3 + 4 of the city;
- 3 - corresponding to areas 1 + 2 of the city;

Next, we built the risk assessment matrix, presented in table 3.

Table 3. Risk assessment matrix

Building	Risk calculation elements				RISK
	Average impact	Danger	Location (areal division)	Exposure	
B1	3	3	area 1	3	9
B2	1,4	1,4	area 3	2	2,8
B3	3	3	area 3	2	6
B4	3	3	area 3	2	6
B5	2,57	2,57	area 3	2	5,14
B6	2	2	area 3	2	4

According to the general recommendations of order 184/1997, 4 risk classes were established, and the buildings taken into study were framed into them:

1 - 3 → low risk - buildings are in an incipient state of degradation, are located in areas with low pedestrian and car traffic and do not present a risk to the population (B2) (green);

> 3 - 6 < → medium risk - the buildings are visibly degraded, they are located in areas with average pedestrian and car traffic, they present a risk to the population in certain conditions (eg: roof tiles dragging), (B5, B6) (yellow);

6 - 8.5 → major risk - the buildings are in an advanced state of degradation, they collapse, they are located in areas with average pedestrian and car traffic, there are frequently reported falls of the constructive elements, outbreaks of infection, the risk to the population is permanent (B3, B4) (orange);

> 8.5 - 9 → extreme risk - the buildings collapse, they are located in areas with heavy pedestrian and car traffic, there are real outbreaks of infection, they were affected by arsons and there is the risk of their extension to neighboring buildings, the risk for population is permanent (B1) (red).

CONCLUSIONS

In order to facilitate the extraction of general conclusions for the present study, we have constructed table 4. In this table a comparison is made between the impact on the urban environment and the risk for the population generated by the abandoned buildings from Petrosani city analyzed in this paper.

Table 4. Comparison between the environmental impact and the risk represented by the abandoned buildings from Petroșani city

Building	The impact over the urban environment	The risk over the urban environment and humans
B1	3	9
B2	1,4	2,8
B3	3	6
B4	3	6
B5	2,57	5,14
B6	2	4

The following can be observed:

- two of the buildings fall into equivalent classes of impact and risk:
 - B1, generates maximum impact and extreme risk (public danger building);
 - B6, generates a medium impact and risk;
- a single building, B2, generates a medium impact and a low risk;
- 2 buildings, B3 and B4, generate maximum impact and major risk;
- a single building, B5, generates a major impact, the risk being medium;

The general conclusion that can be drawn by analyzing table 4 is that abandoned buildings do not always fall into equivalent classes of impact and risk, this fact being strongly influenced by their location (the areal division in which are situated).

Buildings B2, B3, B4 and B5 generate an impact located in a higher class compared to the environmental risk (which is in the immediate lower class) due to aspects related to the positioning of these buildings (the distance to the central area of the city) and to the values of pedestrian and car traffic.

As a result of this study, it can be stated that all these buildings have a negative impact ranging from average to maximum on the urban environment and, with an exception (B2), they present a risk ranging from medium to extreme for the population.

For this reason, part of the abandoned buildings (B1, B3 and B4) must be removed from the urban landscape/environment of Petrosani city (demolished, and the land thus released made available for other purposes), and another part must enter as soon as possible in capital repairs and rehabilitation works.

For buildings B2 and B5 the possibility of their inclusion in the industrial patrimony, restoration and inclusion in a possible urban tourist circuit must be established before is too late.

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ASSESSMENT OF ARSENIC EXPOSURE FROM DRINKING WATER WITHIN A POPULATION GROUP IN COVASNA COUNTY, ROMANIA

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ABSTRACT. Numerous studies have shown that groundwater is naturally contaminated with arsenic exceeding 10 µg/l in the western and central area of Romania. Arsenic contaminated drinking water is a health hazard; therefore, the purpose of this study was to evaluate the exposure to arsenic in drinking water within a population group. In 2014 we recruited 25 subjects from Covasna County, Romania. Participants completed a questionnaire and we collected water samples from drinking water sources (springs and tap) and nail samples. Arsenic concentrations were determined by hydride generation atomic absorption spectrometry. Exposure doses and cancer risk were calculated individually for each subject, following a methodology developed by the US Agency for Toxic Substances and Disease Registry. Arsenic concentrations ranged from 0.5 to 91.8 µg/l, with mean 22.16±37.44 µg/l (mean±SD), in drinking water; and ranged from 0.04 to 100.30 µg/g, with mean 16.90±20.97 µg/g (mean±SD) in nail samples. Exposure doses were above MRL (minimal risk level) for chronic exposure for 3 subjects. Risk estimations predicted a theoretical risk of 5 excess cancer cases in a population of 10,000. Groundwater sources are a potential health hazard for the population in the area, thus due to the limitations of the present study, further studies are needed with extended no of participants and additional individual data.

Key words: *arsenic, drinking water, exposure assessment, cancer risk estimation, Romania.*

INTRODUCTION

Several studies have shown that in some regions of Romania the groundwater is naturally contaminated with arsenic (As). In a pilot study conducted in Arad County, Gelmann et al. (2013) measured inorganic arsenic (iAs) levels in drinking water of $54.4 \pm 27.0 \mu\text{g/l}$ (mean \pm SD). Kunrath et al. (2013) reported average iAs concentrations in water of $40.2 \pm 30.4 \mu\text{g/l}$ (mean \pm DS) in Arad County. Within the Arsenic Health Risk Assessment and Molecular Epidemiology (ASHRAM) study arsenic levels in drinking water were measured between 0.1 and 196 $\mu\text{g/l}$ in Arad County, respectively, between 0.1 and 58 $\mu\text{g/l}$ in Bihor County (Hough et al., 2010; Leonardi et al., 2012). Lindberg et al. (2006) measured the levels of arsenic in drinking water from two counties in Romania: median of 0.48 $\mu\text{g/dm}^3$ and a maximum of 24 $\mu\text{g/dm}^3$ in Bihor County, respectively a median of 0.70 $\mu\text{g/dm}^3$ and a maximum of 95 $\mu\text{g/dm}^3$ in Arad County. Another study conducted in Bihor and Arad counties reported arsenic levels in drinking water between 0 and 176 $\mu\text{g/l}$ (Gurzau and Gurzau, 2001). In a study by Aposhian et al. (2000) water samples were taken from wells in Arad County, from which the study subjects consumed water. The arsenic concentrations measured in the water samples were between 2.8 and 161 $\mu\text{g/l}$. In a study conducted in Timis County, Romania, Bloom et al. (2014) measured drinking water arsenic concentrations ranging from 0.0 to 175.1 $\mu\text{g/l}$, with median 0.4 $\mu\text{g/l}$ and 90thtile 9.4 $\mu\text{g/l}$. Neamtuiu et al. (2015) reported inorganic arsenic concentrations measured in drinking water from sources in Timis County between <0.5 $\mu\text{g/l}$ and 175 $\mu\text{g/l}$, with an average of 8.6 $\mu\text{g/l}$ and a median of 3.0 $\mu\text{g/l}$. Tudorache et al. (2011) measured arsenic concentrations in natural mineral water wells as high as 1505 $\mu\text{g/l}$, in a sampling point in Covasna, Romania and in the central area of Romania the authors found seven mineral water wells containing arsenic at concentrations of ten to a hundred times higher than the allowed limit of 10 $\mu\text{g/l}$. These wells were prohibited for human and animal use (Tudorache et al., 2011).

The data published in the scientific literature regarding arsenic contamination of groundwater in Romania shows that the population in those areas is exposed to arsenic levels higher than the allowed limit of 10 $\mu\text{g/l}$, recommended by the World Health Organization (WHO, 2017).

The purpose of this study was to assess the exposure to arsenic from water in a population group in Covasna County, Romania, by identifying the

sources of exposure to arsenic of the study population, analyzing arsenic levels in groundwater sources from Covasna city and in nail samples collected from the study subjects, by calculating arsenic exposure doses and estimating cancer risks due to exposure to arsenic in drinking water.

MATERIAL AND METHODS

Study population

In 2014 we recruited 25 subjects from the patients of the Cardiovascular Recovery Hospital „Dr. Benedek Geza” from Covasna, Covasna County, Romania. The selection criteria were the following: age between 25 and 80 years; non-smokers or non-smokers in the last 2-3 years; stable housing in Covasna area for the last 10 years; more than 10 sessions of spa treatment at the Cardiovascular Recovery Hospital „Dr. Benedek Geza” Covasna; patients with ischemic heart disease, hypertension and/or arteriopathy; people with diabetes were excluded. The participants were identified by the doctor responsible for the spa treatment. Persons who met the selection criteria listed above were informed about the study objectives and were invited to participate in the study. Those who expressed a desire to participate in this study were offered to sign an informed consent form. Only the persons who signed the informed consent forms were included in the study.

Data on human exposure to environmental pollutants were collected using a questionnaire. Subjects were asked about housing, sources of pollution in the housing area, drinking water consumption, lifestyle, hobbies, habits/behaviors (eg smoking), work history and exposure, and health status.

Drinking water sampling and analysis

Using the questionnaire data, the drinking water sources of the participants were identified. Water samples were collected from 6 mineral springwater sources in Covasna city, a sample from the city's water network and a sample from the water used in the spa treatment of patients. The water samples were collected in 50 ml screw-top decontaminated polyethylene containers, which were previously washed with water and detergent, rinsed

with distilled water and preserved with concentrated analytical grade nitric acid. The samples were labeled with a unique sample identification number and were stored on ice until transfer to the laboratory.

Water samples were analyzed for arsenic concentrations using a Zeenit 700 atomic absorption spectrometer with hydride generation system (Analytic Jena, Germany). The method is based on atomic absorption spectrometric measurement of the arsenic ion content of the sample, generated by the thermal decomposition of arsenic hydride. By this method, only arsenic III (As(III)) can be quantitatively determined, in order to avoid the errors of determination the other oxidation states must be transformed into As(III) before the determination, in order to be able to be transformed into hydride. As(III) is converted to hydride by reaction with sodium tetraborohydride in hydrochloric acid medium. The detection limit of the method was 0.5 µg/l. For digestion 25 ml of the sample was placed in the MARS 5 microwave digester vessel, 4 ml of nitric acid and 12 ml of hydrochloric acid were added, and left for 10 minutes in the microwave digester vessel, stirring occasionally. After the hermetic closure of the vessels, their digestion was started, lasting 20 minutes. After removing the vessels from the oven, they were allowed to cool to room temperature and ventilated to eliminate overpressure. The sample was diluted to 50 ml taking into account the dilutions in the final calculation.

The reduction of arsenic V to arsenic III was achieved by adding 10 ml of concentrated hydrochloric acid and 2 ml of potassium iodide-ascorbic acid to 25 ml of digested sample. It was heated at 50°C for 15 minutes. After cooling, it was brought to level with ultrapure water in 50 ml graduated flasks. In parallel, a control sample was performed using distilled water instead of the sample to be analyzed. The calibration curve was plotted using a standard solution, measuring the absorbance at different concentrations. After the calibration curve was drawn, the samples prepared were atomized in the quartz cell and the absorbance was measured with the Zeenit 700P atomic absorption spectrophotometer. The arsenic concentration, expressed in µg/l, was read directly from the calibration curve taking into account the dilutions made.

Nail sampling and analysis

Nail samples were collected from every subject with disposable metal nail clippers, disinfected with sanitary alcohol, in a quantity of at least 1 g,

from the toes. The nail sample was put into a ziplock plastic bag and labeled with a unique sample identification number. The transportation and storage of nail samples did not require special conditions.

The nail samples were analyzed for arsenic concentrations using a Zeenit 700 atomic absorption spectrometer with hydride generation system (Analytic Jena, Germany). The method is based on atomic absorption spectrometric measurement of the arsenic ion content of the sample, generated by the thermal decomposition of arsenic hydride. By this method, only As(III) can be quantitatively determined, so to avoid the errors of determination, the other oxidation states must be transformed into As(III) before the determination, in order to be able to be transformed into hydride. As(III) is converted to hydride by reaction with sodium tetraborohydride in hydrochloric acid medium.

Nail samples were pretreated; any visible dirt was manually removed, after which the samples were washed five times with ultrapure water, then soaked in acetone for 30 minutes and washed again five times with ultrapure water. Samples were kept in labeled vials, dried in the oven overnight at 50-60°C and dried for 2 hours. The dried samples were weighed and transferred into digestion containers with 5 ml of high purity nitric acid. The digestion process took place in a MARS 5 microwave digestion system, for 20 minutes. After removing the vessels from the oven, they were allowed to cool to room temperature and ventilated to eliminate overpressure. After cooling, each sample was transferred to a 15 ml flask and diluted to 15 ml with ultrapure water.

The calibration curve was plotted using a standard solution, measuring the absorbance at different concentrations. After the calibration curve was drawn, the samples prepared were atomized in the quartz cell and the absorbance was measured with a Zeenit 700P atomic absorption spectrophotometer. The arsenic concentration, expressed in µg/l, was read directly from the calibration curve taking into account the dilutions made. The method detection limit obtained was 0.5 µg/l.

Data analysis

Descriptive statistical analysis of the questionnaire data was performed with MS[®]Excel.

Exposure dose calculation

Arsenic exposure doses via drinking water ingestion were calculated using Exposure Dose Calculator, belonging to the US Agency for Toxic Substances and Disease Registry (ATSDR) of the CDC (Center for Disease Control and Prevention).

Exposure doses from ingestion of water were calculated using the following equation (ATSDR, 2005): $ED = (C \times IR \times EF) / BW$; where, ED = exposure dose [mg/kg /day]; C = concentration of contaminant in water [$\mu\text{g/l}$]; IR = intake rate of water [l/day]; EF = exposure factor (unitless); BW = body weight [kg].

Exposure doses were calculated individually for each study participant taking into account: the source from which the participant drinks water and the arsenic concentration measured in the water sample collected from the respective source, expressed in $\mu\text{g/l}$; the amount of water consumed daily by each participant, expressed in l/day; and the body weight of the participant, expressed in kg.

The exposure dose, expressed in milligrams per kilogram body weight per day (mg/kg/day), is an estimate of the amount of a substance a person comes in contact with, as a result of its activities and habits. Estimating an exposure dose involves determining how much, how often and for how long a person or population may come in contact with a particular chemical, at a certain concentration within a specific environmental factor (ATSDR, 2005). Exposure factor takes into account frequency, duration and exposure time (ATSDR, 2005). Body weight is used in the exposure dose calculation equation to express doses that can be compared within a population. When exposed to the same amount of a substance, people with a lower body weight will receive a relatively higher dose of that substance compared to people with a higher body weight (ATSDR, 2005).

Cancer risk estimation

The risk of cancer from exposure to arsenic in water was estimated according to the ATSDR (Agency for Toxic Substances & Disease Registry) public health assessment guidance manual, using the Exposure Dose Calculator (ATSDR, 2005). According to the quantitative risk assessment

methodology, the exposure doses calculated for the measured concentrations are multiplied by an oral slope factor, calculated by the US Environmental Protection Agency (EPA), to estimate the theoretical risk of developing a malignant tumor as a result of exposure to the substance (ATSDR, 2005). For arsenic the oral slope factor is 1.5 (mg/kg)/day (EPA, 2012).

The equation for calculating cancer risk from exposure to water contaminants via ingestion is as follows (ATSDR, 2005): $CR = ED \times OSF \times (EY/70)$; where, CR = expression of the cancer risk (unitless); ED = exposure dose [mg/kg/day]; OSF = oral slope factor [(mg/kg)/day]; EY = duration of exposure [years].

This calculation estimates a theoretical excess of cancer risk, expressed as the proportion of a population that can be affected by a substance capable of causing the development of a cancer, under the conditions of a fixed duration exposure, in our case, 15 and 30 years of exposure, relative to the average lifespan of 70 years. For example, an estimated cancer risk of 1×10^{-6} predicts the probability of a single additional cancer over background in a population of 1 million people (ATSDR, 2005).

Because of the conservative models used to derive risk factors, the use of this approach provides a theoretical estimate of risk, the actual risk is unknown and may even be zero, according to EPA (ATSDR, 2005). In the case of numerical risk estimates, it should be specified that risk factors are generated using mathematical models applied to epidemiological or experimental data for carcinogenic effects. Mathematical models extrapolate from large experimental doses to small environmental doses. Often, the experimental data represent exposures to chemicals in concentrations with orders of magnitude larger than those that can be found in the environment. In addition, these models often make the assumption that there is no threshold value for carcinogenic effects - a single molecule of a carcinogen is capable of causing cancer. (ATSDR, 2005)

Doses associated with this hypothetical estimated risk may be several orders of magnitude smaller than the doses reported in the scientific literature that would cause carcinogenic effects. As a result, an estimated cancer risk of less than 10^{-6} may indicate that toxicology data will advocate that an excess risk of cancer is more likely to be absent (ATSDR, 2005). An estimated cancer risk greater than 10^{-6} , requires careful review of toxicological data before we venture to assert that there is a potential cancer risk (ATSDR, 2005).

Although we must admit the usefulness of these numerical risk estimates in risk analysis, these estimates must par excellence be viewed in the context of the variables and assumptions involved in their derivation and in the broader context of biomedical opinions, genetic factors and not least, of the exposure conditions (ATSDR, 2005).

RESULTS AND DISCUSSION

Questionnaire data

Study sample characteristics are described in table 1. The study population's (n=25) distribution by gender was uneven, the majority (84%) being female and 16% male. The age and body weight (BW) distribution in the study sample was normal (Age: Kurtosis: -0.04; Skewness: -0.69; BW: Kurtosis: 0.13; Skewness: -0.70). None of the subjects had declared that metal processing or mining industry exists in the area of their residence. The majority (84%) of the subjects stated that the source of water for drinking and cooking is tap water. 16% consume well water, 12% consume spring water with plain water, 24% consume bottled water, while 44% of subjects stated that they consume spring water with mineral water.

None of the investigated subjects currently smoke. 12% of the subjects smoked in the past, on average 9.33 ± 6.03 cigarettes/day (mean \pm SD) for an average period of 11.67 ± 2.89 years (mean \pm SD).

Regarding workplace exposure, one subject stated that he was exposed to pesticides and fertilizers, three subjects stated that they were exposed to chemical disinfectants and one subject to mofetic gas. Interviewed subjects stated that they were not exposed to arsenic, paints or solvents at their workplace.

The data obtained with the study questionnaire showed us that there is no metallurgical industry that involves the use of arsenic in Covasna, so this is not a source of exposure.

Table 1. *Study sample characteristics*

	Mean (%)	SD	Range
Female	(84%)	-	-
Male	(16%)		

ASSESSMENT OF ARSENIC EXPOSURE FROM DRINKING WATER WITHIN A POPULATION GROUP IN COVASNA COUNTY, ROMANIA

Age (years)	59.40	12.38	28-77
Body weight (kg)	74.46	10.24	50-90
Education			
- Primary/professional	(44%)		
- High school/technical school	(39%)		
- University	(17%)		
Pollution sources near residence			
- Traffic	(56%)		
- Dye house	(8%)		
- Waste landfill	(8%)		
- Wood industry	(16%)		
Fuel for heating housing			
- Methane gas	(40%)		
- Wood	(44%)		
- Methane gas and wood	(16%)		
Fuel for cooking			
- Methane gas	(80%)		
- Wood	(4%)		
- Methane gas and wood	(16%)		
Source of water for drinking and cooking			
- Tap water	(84%)		
- Well water	(16%)		
- Spring water (plain water)	(12%)		
- Spring water (mineral water)	(44%)		
- Bottled water	(24%)		
Daily water ingestion (l/day)			
- Tap water (l/day)	5.03	6.87	0-25
- Spring water (mineral water) (l/day)	0.39	0.59	0-2
Consumption of game meat			
- Never	(88%)		
- 2-3 times a month	(8%)		
- once a week	(4%)		
Consumption of fish			
- Never	(56%)		
- 2-3 times a month	(28%)		
- once a week	(16%)		
Smoking			
- Current smoker	(0%)		
- Former smoker	(12%)		

Possible sources of exposure to arsenic in the studied area are: traffic, wood industry, burning of fossil fuels in homes, respectively consumption of spring water. Using body weight information, daily water consumption and drinking water source we were able to calculate the exposure dose and cancer risk individually for each study subject.

Water and nail samples

The average arsenic concentration measured in the nail samples collected from the subjects was $16.90 \pm 20.97 \mu\text{g/g}$ (mean \pm DS), with values ranging from 0.04 to 100.30 $\mu\text{g/g}$.

According to the US Agency for Toxic Substances and Disease Registry (ATSRD, 2013) arsenic levels in nails of unexposed people are ≤ 1 ppm (1 $\mu\text{g/g}$). Only one of the analyzed nail samples had arsenic levels below this level, therefore the results would suggest that the study population was chronically exposed to arsenic. However, it should be noted, that the mass of the samples was not sufficient to determine arsenic concentration by atomic absorption spectrometry with hydride generation, thus the concentrations obtained are higher than the actual level.

The average arsenic concentration measured in the water samples collected from the study area was $22.16 \pm 37.44 \mu\text{g/l}$ (mean \pm DS), with values between 0.5 $\mu\text{g/l}$ and 91.8 $\mu\text{g/l}$.

Two of the samples had arsenic levels higher than the permissible limit of 10 $\mu\text{g/l}$ (WHO, 2017). One of three samples was collected from the bathing water of the hospital's spa treatment facility, which is likely not consumed as drinking water, however there is the possibility of dermal exposure. The other sample with high arsenic level was collected from a spring used as drinking water.

Table 2 presents the results from the scientific literature regarding arsenic levels in water in Romania, compared with the results obtained in the present study.

The maximum arsenic concentration in water determined in the present study is lower than the maximum levels reported in the studies from Arad, Timis and Covasna County, but higher than the maximum levels reported in the studies carried out in Bihor County.

Exposure doses and estimated cancer risk

Arsenic exposure doses via drinking water calculated for the study subjects based on arsenic concentrations measured in water samples collected from the study area, daily water ingestion and body weight declared by the subjects in the questionnaire, are presented in table 3.

Table 2. Comparison of the results obtained with the results from the scientific literature

	Arsenic levels in drinking water ($\mu\text{g/l}$)		
	Mean \pm SD	Min	Max
Present study, Covasna	22.16 \pm 37.44	0.5	91.8
Gelmann et al. (2013), Arad	54.4 \pm 27.0	-	-
Kunrath et al. (2013), Arad	40.2 \pm 30.4	-	-
ASHRAM (Hough et al., 2010; Leonardi et al., 2012), Arad	-	0.1	196
Lindberg et al. (2006), Arad	0.70 (median)	-	95
Aposhian et al. (2000), Arad	-	2.8	161
Gurzau and Gurzau (2001), Bihor and Arad	-	0	176
ASHRAM Hough et al., 2010; Leonardi et al., 2012, Bihor	-	0.1	58
Lindberg et al. (2006), Bihor	0.48 (median)	-	24
Bloom et al. (2014), Timis	0.4 (median)	0	175.1
Neamtiu et al. (2015), Timis	8.6	0.5	175
Tudorache et al. (2011), Covasna	-	-	1505

Table 3. Exposure doses calculated for arsenic levels measured in water samples

Drinking water source	Arsenic exposure dose via drinking water (mg/kg/day)		
	Mean \pm SD	Min	Max
Tap water	3.50E-05 \pm 4.64E-05	0	1.56E-04
Spring water	9.26E-05 \pm 1.79E-04	0	7.16E-04

According to ATSRD (2013) the minimal risk level (MRL) for acute oral exposure to arsenic is 0.005 (5.00E-03) mg/kg/day, calculated based on gastrointestinal effects, respectively the MRL for chronic oral exposure to arsenic is 0.0003 (3.00E-04) mg/kg /day, calculated based on dermal effects. Exposure doses calculated based on the tap water arsenic level did not exceed the MRL for acute and chronic exposure (ATSDR, 2013).

The exposure doses calculated based on the spring water arsenic levels were below the MRL for acute exposure, but in case of three subjects, the exposure dose exceeded the MRL for chronic exposure.

Cancer risks due to arsenic exposure through drinking water was estimated based on calculated exposure doses and are presented in table 4.

In case of exposure to the tap water arsenic levels for 15 years, the estimated cancer risks predict the probability of maximum 5 additional cancer cases over background in a population of 100,000 people. In case of exposure to the tap water arsenic levels for 30 years, the estimated cancer risks predict the probability of maximum one additional cancer case over background in a population of 10,000 people.

Table 4. *Cancer risks estimated based on arsenic exposure doses*

Drinking water source	Exposure period (years)	Mean ± DS	Max
Tap water	15	1.12E-05 ± 1.49E-05	5.02E-05
	30	2.25E-05 ± 2.98E-05	1.00E-04
Spring water	15	2.97E-05 ± 5.73E-05	2.30E-04
	30	5.95E-05 ± 1.15E-04	4.60E-04

The cancer risks calculated for the exposure to arsenic levels in spring water, predict the probability of maximum of 3 additional cancer cases over background in a population of 10,000 people, in the case of an exposure for 15 years, respectively the probability of maximum 5 additional cancer cases over background in a population of 10,000 people, in case of an exposure for 30 years.

The cancer risks estimated in this study were greater than 10^{-6} , which according to the scientific literature in this field (ATSDR, 2005; WHO, 2010; EPA, 2012) suggests that there is a potential excess risk of cancer, but the results must be viewed in the context of the variables and the assumptions involved in deriving them and in the context of the exposure conditions described for this study.

CONCLUSION

The groundwater sources in Covasna, Romania represent a potential health hazard for the population in the area and there is a potential risk of affecting the health of the population, however, due to the limitations of this study, further studies are needed with extended number of participants, more environmental and biological samples and additional individual data.

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PRELIMINARY CONSIDERATIONS REGARDING THE GEOTHERMAL POTENTIAL IN THE APUSENI MOUNTAINS AREA

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ABSTRACT. The Apuseni Mountains have a particular geological structure which gives distinctive geothermal features. They are located between the well-developed geothermal zone of the Pannonian Basin, and the Transylvanian Basin, which is a cold zone. Little information is available in the literature about the geothermal systems from this region. The synthesis of the literature data, combined with our field measurements show there is significant geothermal potential in the area. The thermal water sources are located along a NW-SE alignment. During the field campaigns, the flow rates and temperatures of the water sources were measured. A total flow rate of about 33 l/s was calculated for the study area at an average temperature of about 34 °C. The total thermal energy released by these sources by comparison to the common groundwater is more than 100,000 GJ/year. This geothermal potential could be used as sustainable energy sources for different activities, as agriculture (fish farming, greenhouses), heating (residential and administrative buildings), tourism and balneotherapy.

Key words: *thermal water, geothermal potential, Apuseni Mountains, renewable resources.*

INTRODUCTION

Located between an important geothermal area of Europe (the Pannonian Basin), and a cold structural unit (the Transylvanian Basin), the Apuseni Mts. show distinctive features from the geothermal point of view. Water sources with temperatures between 20 °C and 30 °C in most of the cases, are located on an approximate NW – SE lineament from Beius Depression to the Mures couloir. Although these temperatures are characteristic for the lowest part of the geothermal domain, they reveal a non-negligible heat flux. In the Romanian regulations, as well as in most of the international classifications, geothermal waters are defined as having source temperatures higher than 20 °C (Order No. 87/2008). Some of the investigated waters, although not reaching the 20 °C threshold, show higher temperatures than common groundwater in the study area. We conventionally considered 10 °C as the baseline temperature for groundwater in the investigated area. Although not geothermal waters *sensu stricto*, the waters with temperatures between 10 °C and 20 °C show geothermal influences (Orășeanu, 2016), and were also subject to our investigation.

There is a long history of using the thermal waters in the area for therapeutic or recreational purposes, the *thermae* from Calan (Ad Aquas) and Geoagiu Băi (Germisara) being known since the Roman times (Țentea, 2015; Pricăjan and Airinei, 1981). Currently, there are relatively few studies available explaining the occurrence of these waters and the geothermal potential in the area. An important source of information is the catalogue of the mineral water sources from Romania compiled by the Institute of Balneology and Physiotherapy that includes accurate physical and chemical parameters of the waters (IBF, 1961-1973).

Some other general works area dealing with the geothermal resources of Romania, including the Apuseni Mts. area (e.g. Pricăjan, 1972; Pricăjan and Airinei 1981; Gheorghe and Crăciun, 1993). A more recent synthesis on the karst hydrogeology from the Apuseni Mts. (Orășeanu, 2016) contains relevant information regarding the features of the main geothermal. The most eloquent is the work “Hidrogeologia Carstului din Munții Apuseni” which makes some references to the emergence of geothermal waters in this area. The main geothermal areas noted are: Beiuș Basin, Moneasa area, Rapolt Crystalline Island and Geoagiu Băi.

To the west of the Apuseni Mountains, the Pannonian Basin is a renowned area for its geothermal resources. The geothermal and geochemical features of this basin have been discussed in numerous papers (e.g. Kazmer, 1990; Varsanyi et al., 1997). The Romanian side of the Pannonian Basin corresponds to the Western Plain. This unit also hosts geothermal resources, the water temperature often exceeding 50 °C (e.g. Țenu et al., 1981; Roba, 2010).

The use of geothermal resources is reducing the consumption of fossil fuels, thus contributing to the decrease of the environmental footprint of the human activities. At the national and international level, geothermal energy is considered as a renewable energy source, its use being suitable in the domestic or even industrial systems (Cirstea et al., 2019; Colesca and Ciocoiu, 2013). Worldwide there are numerous examples of such practices in agriculture, energy production, industry, home heating etc. (e.g. Lashen, 1988).

STUDY AREA

From a geological and morphological point of view, the sampling points are located in different structural units (Metaliferi Mountains, Codru Moma Mountains, Cerna-Strei Depression, Brad Depression, Vad – Borod Depression, Beiuș Depression, Sebișului Depression and the Western Hills). The sampling points are distributed along the marginal area of the Apuseni Mountains and in the neighbouring depressions. This distribution is shown in figure 1.

All sampling points included in the present study are listed in table 1. A total of 40 water sources (springs and wells) have been sampled, following an alignment that crosses the Apuseni Mountains from NW to SE. The highest number of sampling points are concentrated in Moneasa area (MA 19, MA 20, MA 21, MA 22, MA 23, MA 24, MA 25, MA 39) Geoagiu area "Rapolt crystalline island" (MA 3, MA 4, MA 5, MA 6, MA 7, MA 8, MA 9, MA 10, MA 11, MA 12, MA 13, MA 14, MA 15, MA 16, MA 38, MA 41) and the northern part of the Beiuș Depression (MA 26, MA 27, MA 28, MA 29, MA 30, MA 31, MA 32, MA 33, MA 34, MA 40).

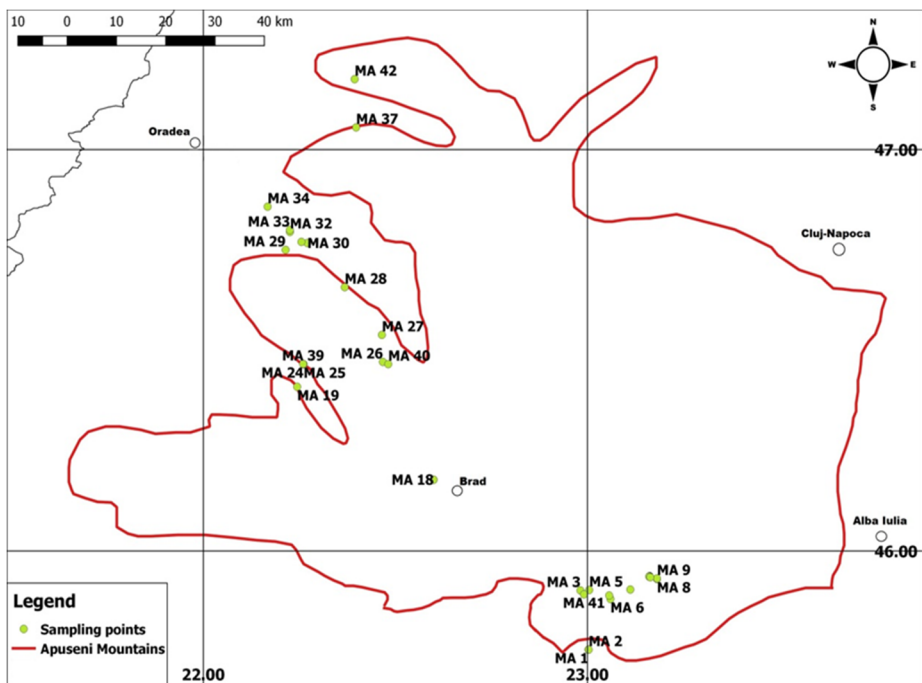


Fig. 1. Geothermal water sampling points.

Table 1. Sampling points from the study area

Sample ID	Site	Coordinates		Sample ID	Site	Coordinates	
		N	E			N	E
MA 1	Calan bai romane	45.754008	23.002722	MA 21	Moneasa 2	46.465350	22.260560
MA 2	Calan izvor	45.754083	23.003277	MA 22	Moneasa 3	46.465350	22.260560
MA 3	Chimindia foraj	45.901611	22.981888	MA 23	Moneasa 4	46.465350	22.260560
MA 4	Chimindia fantana	45.893527	22.983916	MA 24	Moneasa 5	46.465350	22.260560
MA 5	Banpotoc	45.902611	23.004611	MA 25	Moneasa 6	46.464994	22.260939
MA 6	Rapoltel	45.880250	23.060027	MA 26	Vascau	46.470920	22.467360
MA 7	Rovina	45.889000	23.056694	MA 27	Steii (Liceu)	46.538260	22.464880
MA 8	Nătău	45.930250	23.181250	MA 28	Beius foraj 3001	46.657147	22.368027
MA 9	Nătău	45.931500	23.181194	MA 29	Rabagani strand	46.750120	22.213980

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MA 10	Geoagiu izvor 1	45.937166	23.162083	MA 30	Cosdeni cisma	46.767161	22.270719
MA 11	Geoagiu foraj 9	45.936638	23.162083	MA 31	Albesti	46.769990	22.255220
MA 12	Geoagiu foraj 6	45.936416	23.161250	MA 32	Rotaresti cisma	46.794690	22.225380
MA 13	Geoagiu Bai Romane	45.935527	23.161861	MA 33	Rotaresti cazan	46.799540	22.225210
MA 14	Geoagiu supraplin	45.936138	23.161250	MA 34	Ceica	46.857660	22.167220
MA 15	Geoagiu Rozalia	45.936027	23.161000	MA 37	Alesd foraj	47.055180	22.397750
MA 16	Geoagiu foraj 3	45.934527	23.163861	MA 38	La Ferede	45.903788	23.111844
MA 17	Vata Bai 1	46.177480	22.599480	MA 39	Grota Ursului	46.465827	22.259688
MA 18	Vata Bai 2	46.177480	22.599480	MA 40	Vascau Lenin	46.465344	22.481379
MA 19	Dezna	46.408933	22.244202	MA 41	Chimindia ferma	45.891786	22.991069
MA 20	Moneasa 1	46.465350	22.260560	MA 42	Padurea Neagra	47.175319	22.393916

The geological substrate and structural conditions vary for the different sampling points. In this regard, MA 1, MA 2, MA 17 and MA 18 are located on thick Quaternary alluvial deposits.

Points MA 3 to MA 16, MA 38 and MA 41 are located on the border of the Metaliferi Mountains. The area where these points are located has geological characteristics more distinct from the usual ones in the south of the Southern Apuseni Mountains. In the specialized literature it is known as the Crystalline "island" of Rapolt (Ivanovici et al., 1976). At depth, a carbonate complex is well represented, and includes stratified and massive limestone, dolomitic limestone, ankerite, and stratified dolomite (Orășeanu, 2016). The points MA 19 to MA 25 and MA 39 are located in the marginal area of the Codru Moma Mountains. Magmatic rocks as rhyolites occur in the substrate, together with a wide variety of limestones: pink and red limestone, massive and stratified reef limestone, black limestone with sandstone interlayers and massive white limestone containing bauxite intercalations (Ivanovici et al., 1976).

The points MA 26 to MA 34 extend from south to north on the Depression of Beiuș and reach the eastern margin of the Pannonian Basin. This area includes Neogene sedimentary rocks in the substrate (clays, sands, gravels, limestone). Point MA 37 is in the Vad-Borod Depression, with geological characteristics resembling the Beiuș Depression.

MATERIALS AND METHODS

The main water sources with geothermal characteristics have been identified using the published data (Orășeanu, 2016; Pricăjan and Airinei, 1981) etc. The data available for these points were analysed and converted to create a homogeneous database. Subsequently, the points were visualised and analysed by using specific software (Quantum GIS, Microsoft Excel). Water flow and temperatures were measured in the field in 36 points. The water temperature was measured by using a WTW 350i multimeter, while the flow rates were determined by using calibrated vessels, and simultaneously measuring the time. The flow rate was established using the formula: $Q = \Delta V / \Delta t$ (Q-flow; ΔV -volume in liters; Δt -time in seconds).

RESULTS AND DISCUSSIONS

In the context of sustainable development, geothermal energy is regarded as a renewable and environmental friendly energy source. For many areas of the globe, geothermal energy is an important source of energy. However, in the Romanian case, the geothermal resources are not considered a major source of energy.

The potential of geothermal energy in Romania is estimated at 7×10^6 GJ (Colesca and Ciocoiu, 2013). Compared to other renewable energy sources (wind energy, hydroelectric energy) geothermal is considered a rather minor resource, not suitable for producing electricity, due to its low enthalpy. Although, the recent technological developments in thermal energy recovery and use, may increase the interest for this resource.

Table 2. *Geothermal energy in direct use (Source Colesca and Ciocoiu, 2013)*

Field of use	%
Bathing and swimming	42.21%
District heating	38.47%
Individual space heating	8.67%
Geothermal heat pumps	3.59%
Fish farming	2.94%
Greenhouse heating	2.73%
Agricultural drying	0.91%
Industrial process heat	0.49%

Table 2 shows that in Romania the highest amount of geothermal energy is used for recreational purposes in spas and health centres. This type of use is also common in our study area at Călan, Geoagiu-Băi, Moneasa, Felix and Aleşd. This type of use is considered sustainable and has perspectives for development through European Union funding (Surdu et al., 2015). Another significant amount is used for heating the private houses/common spaces with this type of heating agent. The most eloquent example in the area of the Apuseni Mountains is the town of Beiuş, which withdraws the thermal energy needed to heat the homes and public buildings from the thermal aquifer. A low percentage of geothermal energy is used in the primary industrial sector (fish farming, greenhouses), and a similar low percentage is present in the secondary industrial sector (heat for industrial processes).

Table 3. *Geothermal power generation in Romania, Source: (IGA, 2019)*

	Energy	Energy	Energy	Energy	Energy
	TJ/year	TJ/year	TJ/year	TJ/year	TJ/year
Year	1995	2000	2005	2010	2015
Romania	2.753	2.871	2.841	1.265,4	1.905,3

Statistical data presented in table 3 show a significant increase in the use of geothermal energy, especially between 2010 and 2015 (IGA, 2019). Relevant data regarding the confirmed and tested geothermal resources in

the study area were compiled (Pricăjan, 1972; Pricăjan and Airinei, 1981; Orășeanu, 2016; IBF, 1961-1973). A number of 32 thermal groundwater sources including several high-yield drilled wells, give a total flow rate of about 398 l/s at a temperature of 27.97 °C (weighted arithmetic mean). During the field campaigns we identified 40 points with thermal water, and flow rate was measured for most of them (Table 4).

Table 4. Geothermal waters with measured temperature and flow

Sample ID	Site	Temp. (°C)	Flow (l/s)	Sample ID	Site	Temp. (°C)	Flow (l/s)
MA 5	Banpotoc	20.6	0.66	MA 28	Beius foraj 3001	79.8	4.41
MA 6	Rapoltel	23.3	1.77	MA 29	Rabagani strand	23.6	0.87
MA 7	Rovina	21	0.05	MA 37	Alesd foraj	39.6	4
MA 10	Geoagiu izvor 1	28	0.07	MA 38	La Feredee	20.1	0.04
MA 11	Geoagiu foraj 9	28.3	1.09	MA 3	Chimindia foraj	16.0	0.24
MA 12	Geoagiu foraj 6	27.4	0.23	MA 17	Vata Bai 1	10.9	0.15
MA 14	Geoagiu supraplin	31.8	1.53	MA 26	Vascau	11.1	0.66
MA 15	Geoagiu Rozalia	27.5	1	MA 30	Cosdeni cismea	16.5	0.08
MA 16	Geoagiu foraj 3	28.9	2.98	MA 31	Albesti	17.8	0.26
MA 18	Vata Bai 2	32.7	0.4	MA 32	Rotaresti cismea	15.9	0.11
MA 19	Dezna	32.6	0.64	MA 33	Rotaresti cazan	14.6	0.14
MA 20	Moneasa 1	22.8	2.46	MA 34	Ceica	18.5	0.19
MA 21	Moneasa 2	26.3	5.72	MA 40	Vascau Lenin	11.4	0.23
MA 22	Moneasa 3	24.7	0.16	MA 41	Chimindia ferma	14.5	0.81
MA 23	Moneasa 4	25.2	0.38	MA 42	Padurea Neagra	11.2	0.03
MA 25	Moneasa 6	23.8	1.61				

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The examination of data shows a relative homogeneity in terms of temperature. Flows are influenced by the type of exploitation, often the drilled wells having higher flows than the springs. The depth of the drilling directly affects the water temperature. In this case the geothermal gradient should be considered and predictions on the temperature of the aquifers can be made. by using the weighted arithmetic mean for temperature, and summing all measured flows, a total flow rate of 32.97 l/s at average temperature of 34.05 °C was calculated. The thermal contribution from the geothermal resource was calculated as 24.05 °C by respect to the conventionally considered background temperature of groundwater in the area, of 10 °C. The heat input from these geothermal flows is approximately 792,928 calories/s. According to the previously calculated flow rate and geothermal contribution, the generated energy is about 3.31 MJ/s. Annually this energy reaches about 104 455 GJ/year, which is approximately 1.49% of Romania's estimated geothermal potential.

At local scale, a flow rate of 6.9 l/s at average 29.2 °C was calculated for Geoagiu area, totalizing an energy contribution from the geothermal source of about 17,344 GJ/year, while for Moneasa area the flow rate is 10.33 l/s at 25 °C, and the energy contribution is about 20,183 GJ/year.

Table 5. *Geothermal waters with unmeasured flow*

Sample ID	Site	Temp. (°C)
MA 1	Calan bai romane	22.9
MA 2	Calan izvor	28.7
MA 4	Chimindia fantana	14.7
MA 8	Nătău	20.2
MA 9	Nătău	15.9
MA 13	Geoagiu Bai Romane	16.1
MA 24	Moneasa 5	26
MA 27	Steii (Liceu)	44.5
MA 39	Grota Ursului	18.8

For the nine points listed in table 5 the flow measurement was not possible; the arithmetic mean of water temperature is 23.12 °C.

Some of the sources listed in tables 4 and 5 show temperatures between 10 and 20 °C, therefore they are not considered geothermal sources *sensu stricto*, but rather sources with geothermal influence. The amount of energy exceeding the background of groundwater in the area has also been considered. Additionally, these waters represent an indicator for water reservoirs with potentially higher temperature in the depth. These data highlight the diverse and increased potential of the area in terms of geothermal resources.

According to the data presented above, the investigated area of the Apuseni Mountains and the show medium geothermal potential. Although not suitable for the production of electricity, this geothermal potential can be used for other types of activities.

Good examples in the literature show that such sources are suitable for heating greenhouses with vegetables and flowers (Berdondini et al., 1995; Sordelli and Karkoulis, 1995). The lower temperature geothermal fluxes are able to generate optimum temperature for vegetables, for example tomatoes and cucumbers have maximum growth efficiency at temperatures between 20-25 °C (Boyd and Lund, 2000). The thermal fluxes obtained from these sources can be used for processing food (drying) or preparing them for storage (Arason, 2003; Sordelli and Karkoulis, 1995).

Fish farming in geothermal areas is a common practice in several countries. It is well suited for species such as: bass, catfish, salmon, sturgeon, carp, shrimp, crayfish, crabs, oysters, clams, mussels (Boyd and Lund, 2000). In such farms a high growth rate is obtained by eliminating the periods of inactivity for the fish, determined by the cooling of the water. These fish farms can diversify the species grown due to the warm environment that allows the growth of allochthonous species.

Most of the practices and models presented above can be implemented for the Apuseni Mountains area. Considering the positioning of thermal sources in the low and flat areas (Brad Depression, Beius Depression, Cerna-Strei Depression) this energy can be used for greenhouses heating. Fish farms are another viable option for the use of geothermal energy in this area, traditional species such as carp and catfish are suitable for this type of farming.

The rich river network of this area allows the creation of facilities for fish farming that can use a mix between thermal and cold waters. This mix of waters can be adapted according to the requirements of the target species and the season. The use of these resources can create economic opportunities at local and regional level.

CONCLUSIONS

The geothermal water sources sampled within the current study follow an alignment that crosses the Apuseni Mountains from NW to SE. This alignment extends over the territory of three counties (Bihor, Arad and Hunedoara), offering development opportunities to the local administration and communities. Based on field measurements and bibliographic data, a quantitative estimation of the geothermal resources in this area was performed. Potential use of this resource for agriculture (aquaculture, greenhouses) and more extensive heating of residential and administrative buildings is proposed.

Use of these resources represents an economic opportunity for the disadvantaged communities from the area and at the same time an eco-friendly way for the food production. The current uses of thermal water (leisure, heating) can be extended in terms of number of beneficiaries and modern technologies should be implemented in order to increase its efficiency. For the future, this research aims to continue monitoring the area through qualitative and quantitative measurements of geothermal fluxes and creating the premises for investments in the exploitation of these resources.

Acknowledgements

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THE IMPACT OF ROAD TRAFFIC ON THE AIR QUALITY IN CLUJ-NAPOCA: CASE STUDY- NORTH RING ROAD FLOREȘTI – CLUJ-NAPOCA

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ABSTRACT. In this research, we analysed the impact of road traffic on air quality at the Cluj-Napoca border. For this purpose, the road traffic on the North ring road was monitored: Florești (Pădurii Street) - Cluj-Napoca (Donath Street) at the same time with the measurement of the particulate matter PM₁₀. The daily average road traffic was determined according to 'AND 584-2002 normative: "Normative for the calculation of the traffic for the design of the roads from the point of view of the carrying capacity and traffic capacity". For the measurement of particulate matter concentrations PM₁₀, two Dusttrak DRX Aerosol Monitor Model 8533 instruments were used, capable of simultaneously providing mass concentration data for all particle size fractions over a wide range of concentrations (0.001-150 mg/m³) in real time. These were located in two different areas of the ring road: the first instrument was about 20 m from the road on Donath Street in Cluj-Napoca, and the second at a distance of about 80 meters from the road, outside the city.

Key words: *traffic, air quality, PM₁₀, Cluj-Napoca.*

INTRODUCTION AND STUDY AREA

Nowadays talking about air pollution has become trivial and many of us are thinking about countries like India or China when this topic comes up. This is a well-known problem that is getting worse day by day and many of us don't realize it, or simply ignore it (Hsu et al., 2013). It is not necessary for our imagination to carry us so far because pollution exists everywhere, in different forms and from different sources, but it is not to be neglected in a city where the number of inhabitants, constructions and the number of cars is worrying.

The urban air pollution is visible in the morning above the city and often mistaken for fog, which makes us ignore this topic. However, pollution in the urban environment is a serious problem and can lead to various complications and diseases (Donaldson et al., 2000; Pope et al., 2002; Münzel et al., 2017; Saygin et al., 2017; Paraschiv and Paraschiv, 2019). There are many factors that lead to air pollution in urban areas, the sources being multiple (Brunekreef and Holgate, 2002; Marć et al., 2015; Thornbush, M.J., 2015; Stefanie et al., 2015). In this study we analysed the influence of road traffic on particulate matter pollution in the study area.

The road traffic in Cluj-Napoca throughout the year, at different times of the day creates traffic jams on both the main arteries of the city and on ring roads that bypass it. An impressive number of people living in the so-called 'bedroom-localities' commute daily to the city centre, most of them using their own cars as means of transportation.

In previous researches focusing on traffic from Cluj-Napoca in connection with the neighbouring localities, the northern ring road was not taken into account, as it was given into use starting with 2015 (as an agricultural road), today being a vital alternative for the thousands of commuters who use it daily.

The northern ring road that connects Grigorescu neighbourhood from Cluj-Napoca with Florești village is one of the busiest streets in the city in the rush hours, due to a big share of the more than 10,000 commuters and students who go daily to Cluj-Napoca. The accelerated population growth in Floresti commune (35,118 official inhabitants in 2018) made it the largest peri-urban locality in Romania. Thus, Floresti has the biggest difference between the share of the active population working in another city than the one where they are residents (52.06% of the active population from Florești are working in Cluj-Napoca). In figure 1 the location of the measuring instruments is marked with a +.

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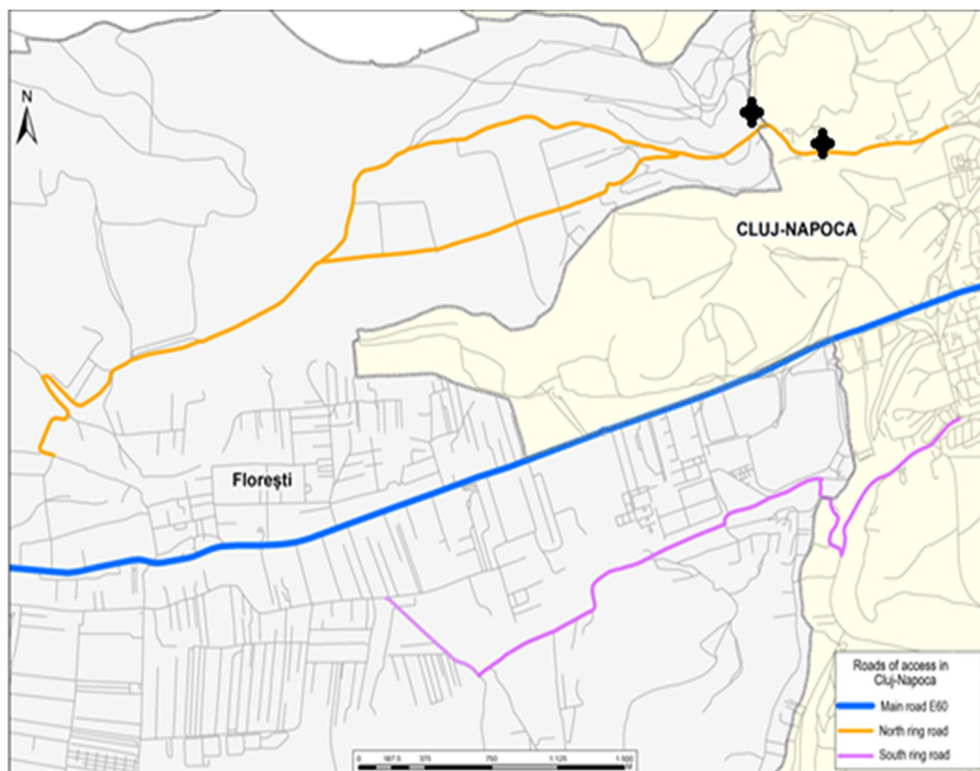


Fig. 1. Location of the study area

MATERIALS AND METHOD

The study's stages were divided into: bibliographic documentation (theoretical and mapping), monitoring the traffic and measuring the PM_{10} and $PM_{2.5}$, and data analysis. The traffic monitoring supposed the observation and counting the vehicles in traffic at certain time intervals for one week. The PM_{10} and $PM_{2.5}$ concentrations were measured between 14 and 30 of March 2019 using two Dusttrak DRX 8533 instruments at two different locations on the ring road as seen in Fig. 1: the first instrument was located about 20 m from the road, on Donath street in Cluj-Napoca, and the second at a distance of about 80 meters from the road, on Padurii street outside the city.

The DustTrak DRX 8533 optical instrument can simultaneously analyse PM₁₀, PM₄, PM_{2.5}, PM₁ and total fraction concentrations. The DustTrak DRX is a battery-powered analytical instrument providing real-time interpretation of aerosol mass. By using this instrument, the aerosol is drawn into the detection chamber in a continuous flow using a diaphragm pump. A part of the aerosol stream is separated before the detection chamber and passed through a HEPA filter to be re-injected into the chamber around the inlet nozzle. The remaining flux, called the standard flow, passes through the inlet nozzle into the detection chamber where it is illuminated by a laser consisting of a diode. In the first phase, the light emitted by the diode passes through a collimating lens and then through a cylindrical lens in order to create a thin layer of light. A golden spherical mirror retains a significant fraction of the light scattered by particles and concentrates it into a photodetector. However, signal processing is very different from an usual photometer. Although the voltage in the photodetector, which is proportional to the mass concentration, is used to determine the aerosol concentration, the individual pulses are also used for measuring the individual particles (TSI Incorporated, 2019).

For one week, the traffic was monitored on Donath Street to and from Floresti, every day, at certain hours between 7:00 and 21:00. In total there were 21 hours, of which 15 on business days and 6 hours on weekends. The daily average road traffic was determined according to 'AND 584-2002 normative: "Normative for the calculation of the traffic for the design of the roads from the point of view of the carrying capacity and traffic capacity".

RESULTS AND DISCUSSION

All the cars that crossed in both directions at the monitored timeline have been counted. Also the number of passengers in each car was considered. From the time interval during the weekend which overlapped with the one during the week (7:00 - 8:00, 8:00 - 9:00, 14:00 - 15:00, 17:00 - 18:00, 18:00 - 19:00, 19:00 – 20:00) it turned out that only 21% of the cars were circulating in weekend and 79% during the weekdays.

As assumed, the highest numbers of cars in traffic are in the morning and afternoon rush hours with a peak of more than 1000 cars/hour at 07:00 (see figure 2).

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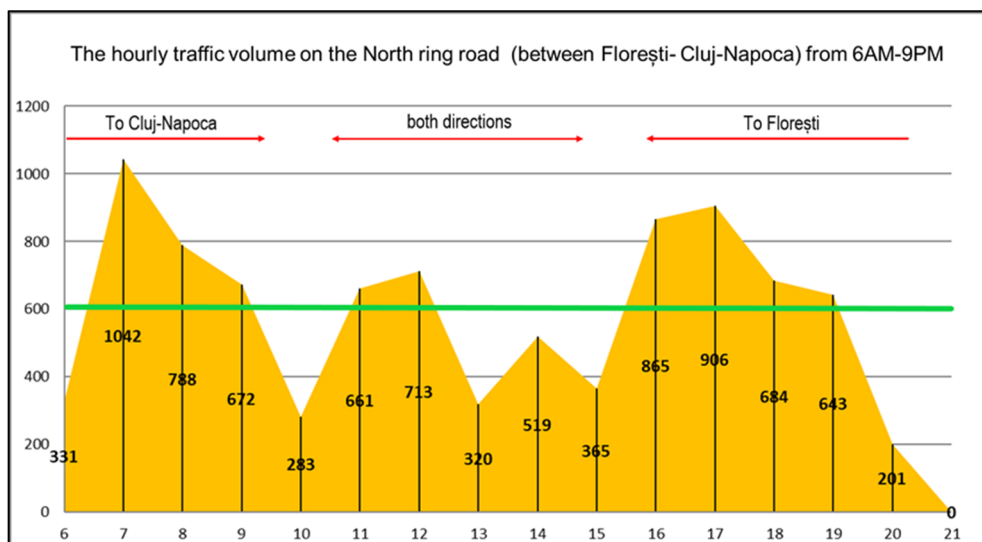


Fig. 2. The hourly traffic volume observed in the study area

Out of the counted cars, in working days in 54.3 % of the cars was only the driver, 33.7 % had two people, 8.6 % three people, 2.3 % with four people and 1% with 5 or more people. During the weekend, 41.8% of the cars had 2 people inside, in 40.9% was only the driver and the hierarchy then continues as in the first case. The low number of people in cars is one of the reasons of traffic jams but also of the high degree of pollution, not only in the studied area but perhaps worldwide. People choose to use their personal car in the first place for comfort, and also due to the insufficient means of public transportation with regular trips between the two localities (Cluj-Napoca - Florești) during the rush hours.

As seen in figure 3, on Donath Street, inside the city, the PM₁₀ concentrations are higher than at the periphery of the city, on Pădurii Street for almost the entire monitored time interval.

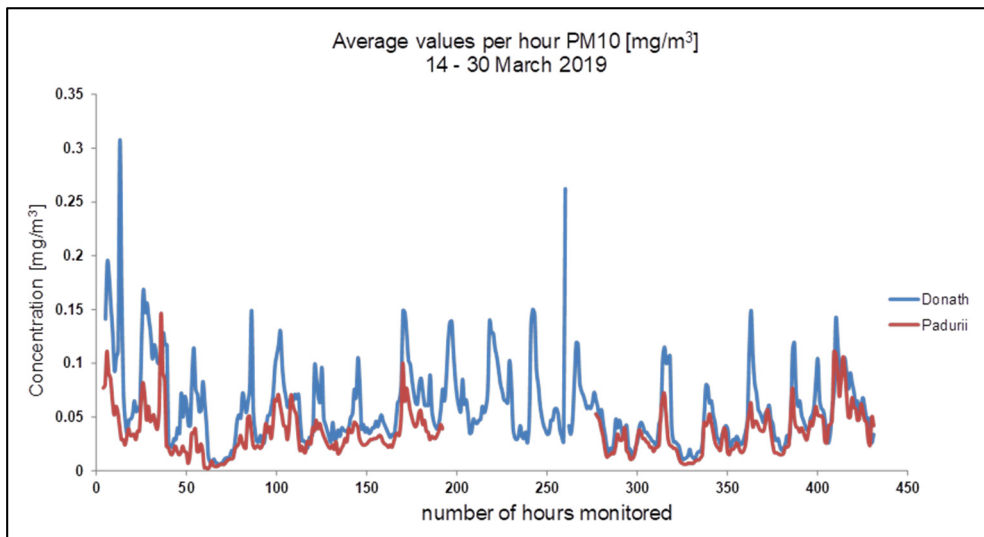


Fig. 3. Average hourly values for PM_{10} particles measured between 14-30 March 2019

The maximum PM_{10} daily limit value according to the European and national legislation for the protection of human health is $50 \mu\text{g} / \text{m}^3$ (Law no. 104/2011).

As seen in figure 4, the daily average values for the time interval in which the measurements were made are usually higher than the limit value of $50 \mu\text{g}/\text{m}^3$ on Donath Street and do not exceed the limit on Padurii Street. The lack of data at the second instrument is due to a power shortage affecting the instrument. Also 2 rainy episodes were observed on day 3 and on day 14, the PM_{10} concentration being lower after them.

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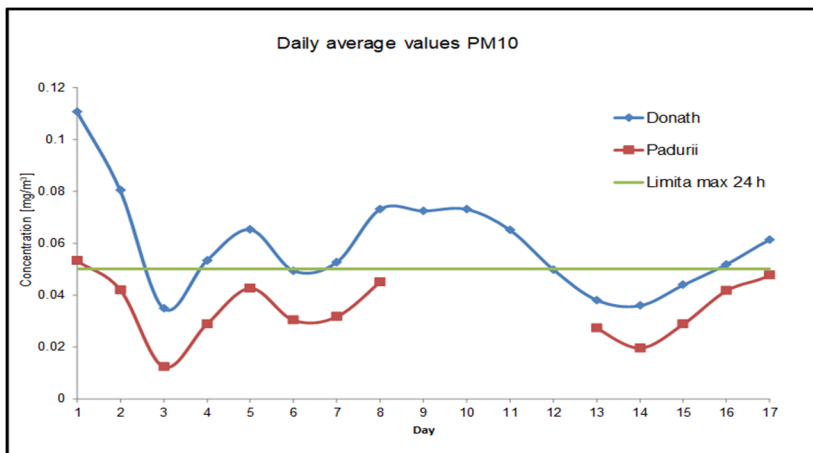


Fig. 4. Average values of PM₁₀ particles for the monitored period

Figure 5 shows the variation of PM₁₀ concentration for each hour monitored during the week in which the traffic was observed as well. Although an increase in concentrations can be observed in the morning hours and then towards evening, the correlation with the number of cars on the analysed route was low ($r = 0.06.$).

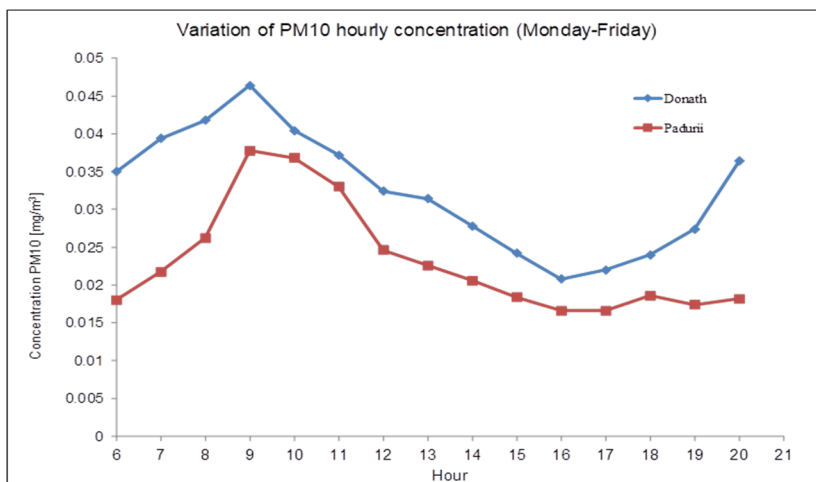


Fig. 5. Variation of PM₁₀ hourly concentration

On the analysed route, at the sites where the instruments were located, it seems that the general urban background has a greater influence than the local traffic.

CONCLUSIONS AND PROPOSALS

In this paper we analysed the impact of road traffic on air quality at the North ring road between Florești (Pădurii street) and Cluj-Napoca (Donath street), Romania.

In this research, we analysed the impact of road traffic on air quality at the Cluj-Napoca border. For this purpose, the road traffic on the North ring road was monitored: Florești (Pădurii street) - Cluj-Napoca (Donath street) at the same time with the measurements of the particulate matter PM₁₀. The north ring road was transformed from a simple agricultural road into an important artery of the city with more than 1000 cars/hour at the rush hours, having a negative impact in terms of time spent in traffic and agglomeration in the narrow adjacent streets and also on level of noise in the area.

We measured the PM₁₀ concentrations between 14 and 30 of March 2019 at two sites near the road, one in the city and the second in the suburban area of the city. Also the traffic was monitored for one week overlapping the PM₁₀ concentrations measurements. The results did not indicate any correlation between the road traffic and PM₁₀ concentrations. Nevertheless, the values measured inside the city, on Donath Street are usually higher than the daily limit values. The main cause for the local pollution seems to be the urban background.

Given the fact that thousands of people need to travel daily from Florești to Cluj-Napoca and vice versa, to ban the use of this road for commuters is inappropriate. In order to reduce the local noise and PM₁₀ pollution, several recommendations could be implemented, resulting in the time economy and improving the economic aspects. The first proposal refers to the use of car-sharing apps, considering that over 50% of the vehicles monitored were occupied only by the driver. Large scale using of such applications would reduce the costs, the number of cars, the time spent in traffic and also the noise and air pollution. Another proposal is to facilitate the entry on the market of private transport companies for students. One of the main reasons for traffic jams between 7:00 – 9:00 and 16:00- 19:00, is the displacement of thousands of students between Florești and Cluj-Napoca city.

The South Metropolitan Ring Road will ease the traffic and also reduce the pollution. Its route starts from Gilău area and intersects the Transylvania Highway, then follows the Someș River, enters Cluj-Napoca in the Cora area, then reaches Bucium and St. Ion forest areas. It crosses the south of Mănăștur, Zorilor, Bună Ziua and Gheorgheni neighbourhoods, goes through Someșeni and enters the extension of Bulevardul Muncii, near the airport. In the Florești area are planned three interchange points with the metropolitan road, in the area of Izlazului streets (entrance from Luna direction), Tudor Vladimirescu and Plopilor in order to catch the daily flows to Cluj-Napoca where there will be six interchange points. By implementing this project Cluj-Napoca and the western area of the municipality will be relieved of transit traffic, and the decongestion of traffic will lead to lower values of PM₁₀.

Other solutions that can be implemented by local authorities are referring to the setup of a separate lane for public transportation on the European road E60 and implementation of bike sharing-projects and at the same time building of the necessary infrastructure.

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ALUMINIUM CANS WASTE MELTING IN MICROWAVE FIELD

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ABSTRACT. Recycling of aluminium, particularly aluminium beverage cans is important due to several economic and environmental reasons. Aluminium beverage cans are by far the most recycled consumer beverage packages globally, by units, weight and percentage recycled. It amounts to more than twice the recycling rate and recycled content percentages for beverage packages of other materials. Recycling of aluminium requires only 5-10% of the energy for primary aluminium production. In this paper, the melting of cans wastes in microwave furnace as well as the treatment of noxious emissions in a microwave thermal filter has been preliminary investigated. Melting temperature, composition of the melting - protection fluxes as well as waste/flux ratio on the metal recovery efficiency have been investigated. During the cans waste melting, due to the burning of paint and lacquer coatings, environmental toxic compounds such as: volatile organic compounds (VOCs) (acetone, benzene, ethylbenzene, styrene, toluene, etc.) have been detected in the effluent gases. The treatment was carried out by passing the gases through a microwave susceptor granular material filter (SiC balls), placed in a microwave transparent tube. It was observed that the temperature of the filter has a major influence on the neutralization of the toxic compounds, the content in the gases being reduced below the legal limits.

Key words: *aluminium cans waste, microwave melting, toxic compounds, thermal filter.*

INTRODUCTION

The recycling of aluminium is an important activity in the context of sustainable development and environmental protection, due to its economic and environmental potential. A high percent of drink cans are made of aluminium; while almost all food cans are made of steels, aluminium unique properties make it adequate for holding carbonated beverages.

Aluminium beverage cans are the most recycled packaging materials because of the high value of the wastes globally produced, but also because this process is useful in saving energy and reducing emissions (Appleton et al, 2005).

In this paper is investigated the melting process of the aluminium beverage cans in the microwave furnace. Microwave melting is a novel technology which presents a series of major advantages compared to the classical pyrometallurgical processes, such as simultaneous evolution of the heating gradient in the entire volume of material, a much higher heating rates (Capuzzi and Timelli, 2018) that shorten the melting time by 70-85%, allowing energy savings (Verran and Kurzawa, 2008) and higher processing capacities and a superior quality of the obtained materials by reducing the melt impurification through oxidation. Microwave heating also offers the possibility to neutralize the gaseous emissions by passing the gas through a granular microwave susceptor material thermal filter (Das and Hughes, 2006; Gupta and Wong, 2007; Chandrasekaran et al., 2011).

EXPERIMENTAL

The experimental microwave equipment for melting the aluminium beverage cans is presented in figure 1. It consists of a cylindrical enclosure made of steel (1), in which are five rectangular windows for mounting the microwave magnetrons (6). The axes of the windows are positioned in different horizontal planes, the angle between the axes is 72° , thus radiating different areas of the susceptor material (3). In order to reduce the heat loss,

the interior of the enclosure is covered with a thermal insulation layer (2) made of super-alumina ceramic fibres with resistance to temperatures up to 1600°C. Coaxial, there is placed the melting crucible (4), made of graphite-clay mixture, approx. 1 litter capacity, clothed in a microwave susceptible material (3) made of silicon carbide. The batch heating is performed by five 2.45 GHz microwave generators (6) of 850 W maximum power. The temperature is measured using a ceramic sheath K-type thermocouple (8).

Generated harmful gases and dust are captured through the exhaust pipe (9), fixed in the furnace cover (7), and which is connected with the gas treatment thermal filter (11). The filter consists of a steel cylinder in which windows are cut out for the installation of three 2.45 GHz magnetrons (13) of 850 W power. A microwave transparent quartz cylinder is placed inside the steel cylinder and contains a microwave susceptible material SiC (12) in the form of 5-10 mm diameter granules. The temperature inside the thermal filter is measured with a K-type thermocouple. Gas and dust sampling are carried out through nozzles (10, 14) attached to the exhaust tube (9) just before and after the filter.

The laboratory MW experimental non-ferrous waste melting installation is presented in figure 2.

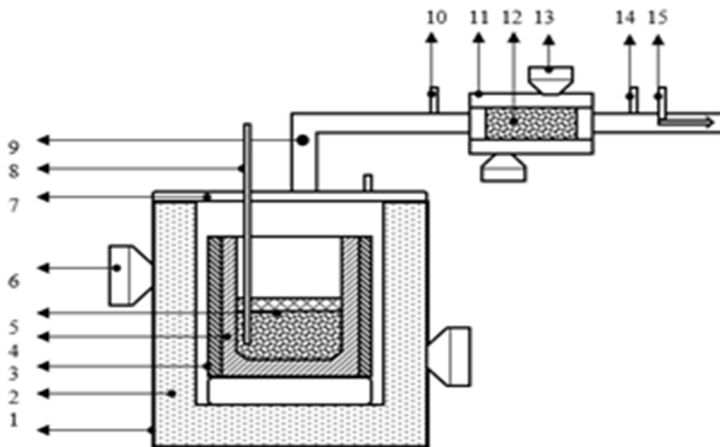


Fig. 1. Microwave melting furnace and gases thermal filter

1. Furnace body (steel);
2. Thermal insulating material;
3. MW susceptor material (SiC);
4. Melting graphite crucible;
5. Charge (Al cable waste + cover flux);
6. Furnace MW magnetrons;
7. Furnace cover (steel);
8. Thermocouple (K-type);
9. Flexible exhaust tube (steel);
- 10, 14. Gas sampling socket pipe;
11. Burning gases thermal filter treating;
12. MW susceptor material (SiC balls);
13. Filter MW magnetrons;
15. Compressed air tube



Fig. 2. Laboratory microwave furnace and gases thermal filter installation

In order to protect the metal bath and reduce the metal losses through oxidation, during the melting process of the aluminium beverage cans are used fluxes or fusing agents (in liquid or solid state). The fluxes have an important role in decreasing the melting interaction with gases from the microwave furnace atmosphere and the fusing agents can refine and purify the melting, or modify the casting structure. In the experimental work, the used fluxes were NaCl, KCl, NaF, CaF₂ and cryolite. In table 1 are presented the compositions of the fluxes used for aluminium alloys.

Table 1. Compositions of the fluxes used for aluminium beverage cans melting

Code	NaCl	KCl	CaF ₂	NaF	Cryolite Na ₃ AlF ₆
FL 1	35	35	15		15
FL 2	50	50			
FL 3	45	45		10	
FL 4	40	40			20

In establishing the chemical composition of the fluxes, there must be taken into consideration the price of the components and the ratio between the efficiency and the price of the expensive elements on the productivity of the industrial metals/alloys waste recovery process (Liu and Muller, 2012).

ALUMINIUM CANS WASTE MELTING IN MICROWAVE FIELD

According to the information provided by CanPack manufacturer, the aluminium beverage cans are produced using AlMn1Mg1 alloy. In table 2 is presented the chemical composition and in table 3 are presented the technical data of the aluminium beverage cans.

Table 2. *The chemical composition of the aluminium beverage cans*

El.	Mn	Mg	Fe	Si	Cu	Zn	Others	Al
%	1-1.5	0.8-1.3	Max. 0.7	Max. 0.3	Max. 0.25	Max. 0.25	Each 0.05	rest
gr.							Total 0.15	

Table 3. *Technical data for aluminium beverage cans*

Beverage can weight (500ml)	Exterior paint/Interior protection polish	Al alloy
16.8 – 17.2	3-4.5% (for efficiency can be considered 4%)	rest (96%)

The aluminium beverage cans (figure 3) were dried for 30 minutes in stove, on a temperature of 60°C, to eliminate the residual humidity. After drying, the beverage cans were manual and mechanical pressed. In experiments, the number of aluminium beverage cans were almost 12/charge, the total mass was of 200 – 203g and the quality of used flux was of 40g/charge (20% from the waste charge).



Fig. 3. *Aluminium beverage cans*

The obtained experimental data, regarding the mass of the aluminium beverage cans introduced in the microwave furnace, flux and the obtained ingot are presented in table 4.

Table 4. *Experimental data regarding the melting of the aluminium beverage cans in the microwave field*

Exp. code	Charge	Flux, 40 g	Temp. [°C]	Crucible	Obtained materials, [g]			η_{rec}
	Al beverage cans mass, g				Metallic ingot	Metal granule	Slag	
DA1	203.1	F1	700	SiC	141.2	40.1	40.4	72
DA2	201.7	F1	700	Graphite	136.8	49.5	30.4	70
DA3	202.4	F1	750	SiC	163.2	28.8	73.9	80
DA4	202.8	F1	750	Graphite	170.9	16.3	46.9	87
DA5	200.3	F1	800	SiC	147.5	31.4	76.8	76
DA6	201.5	F1	800	Graphite	150.8	27.2	68.1	78
DA7	201.2	F2	750	SiC	147.8	19.3	42.5	76
DA8	200.8	F2	750	Graphite	149.3	21.4	38.8	77
DA9	202.3	F3	750	SiC	152.4	16.8	47.2	78
DA10	201.6	F3	750	Graphite	158.2	20.5	31.5	82
DA11	200.5	F4	750	SiC	165.7	21.2	43.8	86
DA12	203.4	F4	750	Graphite	173.5	19.4	50.7	88

In figure 4 are presented the aluminium recovery output, depending on the working temperature and the crucible material, using a F1 flux and in figure 5 is represented the aluminium recovery output for 750°C working temperature.

ALUMINIUM CANS WASTE MELTING IN MICROWAVE FIELD

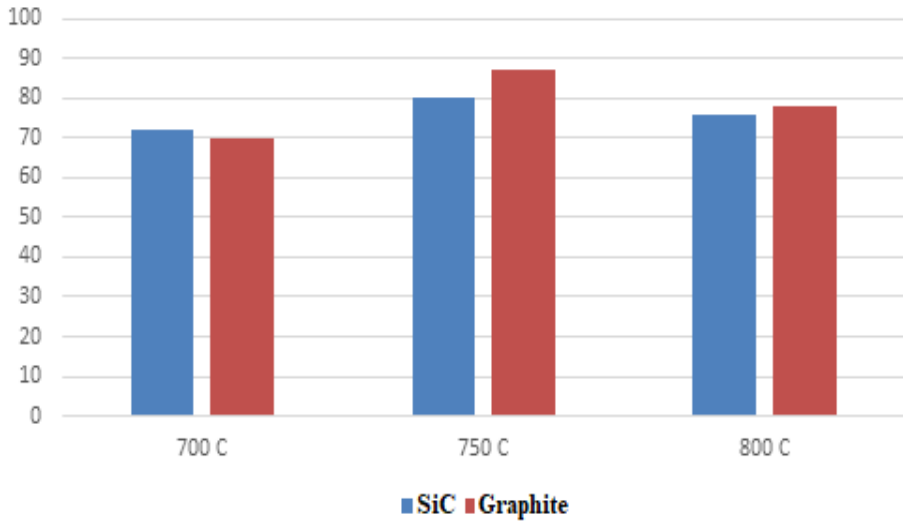


Fig. 4. Aluminium recovery output, using F1 flux

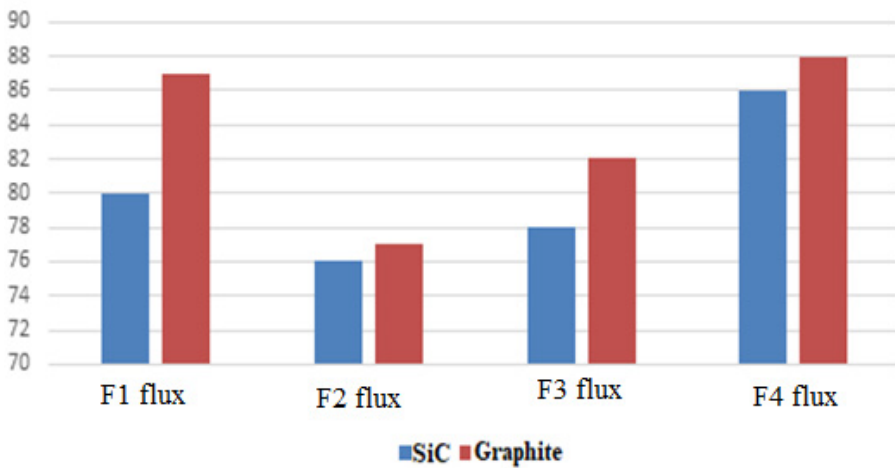


Fig. 5. Aluminium recovery output on 750°C, depending on the melting flux composition and the crucible material

After the melting process of the aluminium beverage cans in microwave field were obtained aluminium ingots (table 5) and slag (table 6), which were analysed in laboratory.

Table 5. Chemical composition of the ingots obtained on the melting process of the aluminium beverage cans

Exp. code	Cu	Fe	Mg	Mn	Pb	Si	Ti	Zn	Al
DA4	0.146	0.376	0.86	0.77	0.038	0.084	0.014	0.047	base

Table 6. Chemical composition of the slags obtained on the melting process of the aluminium beverage cans

Exp. code	Al	Si	Cu	Mg	Pb	Zn	Sb	Sn	Other
DA4	27.70	18.50	0.35	0.10	0.018	0.13	0.005	0.016	rest

In figure 6 can be observed the aluminium metallic ingot and slags obtained on the melting process of the aluminium beverage cans.

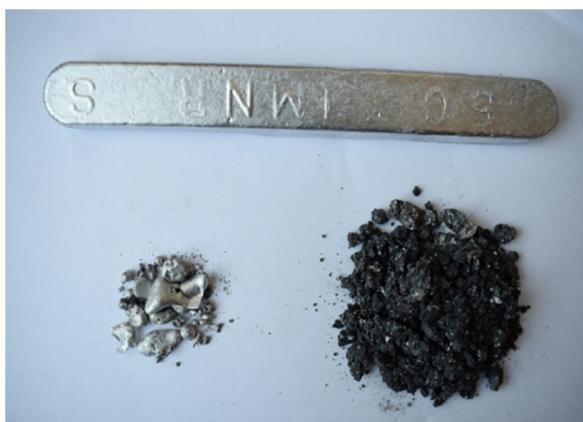


Fig. 6. Aluminium metallic ingot and slags obtained on the melting process of the aluminium beverage cans

The harmful gases generated in the melting process of the metallic wastes in the microwave field (Sun et al., 2005) were treated using a thermal filter (figure 2) containing three magnetrons. For example, the volatile organic

compounds (Van der Harst et al., 2016) were determined before and after passing through the thermal filter using aluminium beverage cans and 40g or 60g of flux or on different temperatures: 660°C and 700°C (table 7). There can be observed different values of the total amount of the volatile organic compounds, due to the thickness and composition of the paint layer applied by aluminium beverage cans manufacturers.

Table 7. Volatile organic compounds (VOC) measurements before and after treating in the thermal filter (B f – before filter treatment; A f – after filter treatment)

	DA 2		DA 4		DA 6	
	B f	A f	B f	A f	B f	A f
VOC	94.6	4.28	85.9	1.08	137.58	0.46
Ethanol	8.09	0.21	10.45	-	15.04	-
Acetone	14.78	1.43	17.76	0.58	20.68	0.46
2-Butanone	0.69	-	0.97	-	1.70	-
Benzene	15.30	1.17	15.24	0.5	20.65	-
Butanol	4.51	0.21	2.94	-	5.95	-
1,4-Dioxane	1.39	-	1.0	-	1.65	-
Toluen	15.22	0.52	9.9	-	17.57	-
Ethylbenzene	7.69	-	5.34	-	11.96	-
Xylene	3.75	0.59	2.55	-	4.07	-
Styrene	19.01	0.15	15.94	-	29.28	-
1-Methylethylbenzene	1.72	-	1.33	-	3.01	-
Propylbenzene	0.63	-	0.67	-	1.31	-
Trimethylbenzene	0.30	-	-	-	0.31	-
Izopropyltoluene	1.53	-	1.83	-	4.39	-

CONCLUSIONS

The recycling of aluminium, particularly aluminium beverage cans is an important environment and economic activity, in the context of sustainable development of industry. In the article was presented the melting process of

the aluminium beverage cans in the microwave furnace, due to technological advantages, compared to the classical pyrometallurgical processes. The preliminary experiments demonstrated that the microwave melting of the compressed aluminium beverage cans, as well as the microwave thermal filter treating of gaseous emissions are reliable methods. There were obtained aluminium ingots, which can be reintroduced in the economic circuit.

Due to the thermal decomposition of the paint layer, which is applied on the surface of the aluminium beverage cans, harmful compounds such as benzene, toluene, ethylbenzene, xylene, HCl, etc. have been determined in the effluent gases.

The gaseous emissions were treated in a microwave thermal filter, in order to reduce their concentration below the legal limits. It was observed that the temperature of the filter has a major influence on the neutralization of the toxic compounds (benzene, HCl).

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